Life Cycle Assessment of Natural Gas Utilization in Light-duty Passenger Vehicles

by

Qiang Dai

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Environmental Engineering)
in the University of Michigan
2014

Doctoral Committee:

Associate Professor Christian M. Lastoskie, Chair
Assistant Professor Bart Bartlett
Professor Victor C. Li
Associate Professor Shelie Miller

Dedication

To my grandfather
for making me who I am

Wish you could share this accomplishment with me

Acknowledgements

This dissertation research project was made possible by financial and technical support from Michigan Economic Development Corporation, Center of Energy Excellence and Sakti3. I'm grateful to have the opportunity to work on such a mind-opening project to expand my knowledge base and establish myself in my chosen field of study.

PhD study is not plain sailing for me, and I made it through thanks to the help of many people. First and foremost, I'd like to thank my advisor and chair, Dr. Christian Lastoskie, for guiding me through my ups and downs, for providing prompt and constructive comments and feedback to my work, and for preparing me to be a better researcher and teacher. I'd also like to thank my committee members: Dr. Bart Bartlett, Dr. Victor Li and Dr. Shelie Miller, for your valuable time and inputs which notably improve this dissertation, both in scope and depth. My fellow graduate students, especially my research group mates, thank you for the encouragement, collaboration, and witty chitchats. Last but not least, thank you dad, for raising me to be successfully independent; thank you mom, for your unconditional love and support; and thank you, my friends, for keeping me sane, happy and accompanied.

Table of Contents

List of Figures

List of Tables

Abstract

Natural gas has long been considered a cleaner fuel than coal and petroleum. With the advent of new natural gas extraction technologies, such as horizontal drilling and hydraulic fracturing, and more stringent future Corporate Average Fuel Economy (CAFE) and vehicle emission standards, a dramatic increase in the use of natural gas and its chemical derivatives for mobility needs has been predicted for the next few decades. Therefore, the environmental impacts associated with the delivery of driven vehicle miles are worth investigating for the alternative modes of natural gas utilization in the transportation sector.

Although alternative fuel vehicles and their environmental performances have become the focus of life cycle practitioners in recent years, to date, no research has been done to compare the life cycle impacts of delivering mobility using the same fuel resource for different personal passenger vehicles, especially when this resource comes to natural gas. In this study, the environmental impacts of delivering driven vehicle miles are evaluated using life cycle assessment (LCA) for three different fleets, each powered either directly or indirectly by natural gas. The fleets studied are battery electric vehicles (BEVs) using electricity generated from natural gas combined cycle (NGCC) power plants; Compressed natural gas vehicles (CNGVs), which are internal combustion vehicles modified to burn compressed natural gas; and fuel cell vehicles (FCVs) powered by hydrogen produced from steam methane reforming of natural gas.

To better understand the environmental friendliness of the three mobility means, we first investigate the manufacturing phase of BEVs. We find that the lithium ion battery (LIB), the energy source of BEVs, accounts for a substantial fraction of the total life cycle impacts of BEVs, mainly due to the extraction of transitional metals, especially nickel and cobalt, involved in the synthesis of active cathode materials for LIBs. Use of organic solvents and energy consumption in the synthesis processes are also environmental hot spots in the BEV manufacturing phase. We then move down the life cycle stages and examine the use phase. We observe that use phase is the single largest contributor to the environmental impacts of BEVs. We also find that in addition to the switch to a greener electricity mix, improvements in cathode materials electrochemical properties, such as cycle life and specific energy, would be the key to a more sustainable transportation mode by BEV. Then we expand the system boundary and investigate CNGV and FCV. The results reiterate the dominance of use phase and the importance of vehicle energy sources in the life cycle environmental footprints of the three mobility means. When comparing the three mobility means, we find that both BEV and FCV are promising alternatives to conventional internal combustion engine vehicles due to higher overall energy conversion efficiency. Finally, we apply Wright's law to major technology performance metrics to model technological progression and temporal variations associated with the LCA study. We find that advances in technology and legislation could be the game changer in terms of determining the most environmental benign personal transportation means.

The dissertation is the first LCA study to systematically compare different transportation means powered by natural gas, and it’s also the first to incorporate technological advances together with temporal variations into LCA. It provides insight into which mode of natural gas-based personal passenger mobility offers the most compelling future environmental benefits, as both the civil power infrastructure and the transportation sector undergoes a greening transition, from coal and petroleum respectively, to natural gas.

Chapter 1

Introduction

1.1 Booming of Natural Gas and Its Potential Role in Future Transportation Sector

Natural gas has long been considered a cleaner fuel than coal and petroleum, yet its higher cost has hindered its deeper penetration into energy markets. Shale gas plays, although prevalent in the lower 48 states of U.S., pose substantial difficulties to natural gas explorers, as they are usually impermeable to gas flows except when natural or artificial fractures occur. The advent of new technologies, such as horizontal drilling and hydraulic fracturing, has made profitable production of shale gas possible.

Considering that among the 862 trillion cubic feet (tcf) of shale gas resources that are technically recoverable, only 1-3% has already been produced, a great possibility for future shooting up of shale gas production is lurking on the horizon[1]. According to the statistics and predictions of U.S. Energy Information Administration (EIA), from 2000 to 2006, production of shale gas in the U.S. grew by an annual average of 17%. From 2006 to 2010, U.S. shale gas production maintained an annual growth of 48 percent. Moreover, a 113% increase in the total production of shale gas from 2011 to 2040 is predicted in the *2013 Annual Energy Outlook* (Figure 1-1) [2].

The rapid increase in natural gas production in the next few decades will surely have significant impact on future U.S. energy composition. As a result of its low cost and low carbon dioxide intensity, in conjunction with growing electricity demand under the upcoming retirement of 39 GW of existing capacity, natural gas is expected to fire 60% of 223 GW new power plants added between 2010 and 2035[1] (Figure 1-2). Moreover, according to the projection of dry natural gas consumption by sector, as depicted in Figure 1-3, the consumptions in sectors of electricity generation and transportation are expected to double from year 2005 to 2040[2].

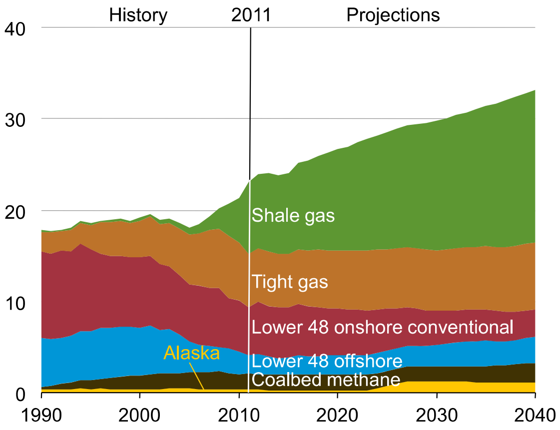

Figure 1-1. Natural gas production by Source, 1990-2040 (Source: EIA)

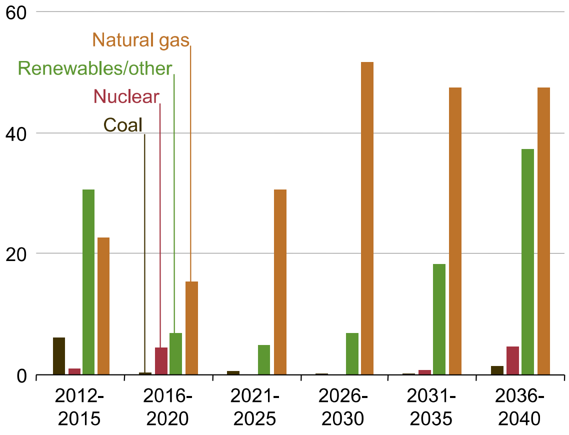

Figure 1-2. Electricity Generation Capacity (GW) Addition by Fuel Type, 2012-2040

1.2 Natural Gas Powered Mobility Options

Thinking of the projection of significant growth of unconventional light-duty vehicles up to 2035 (Figure 1- 4), and the fact that battery-powered electric vehicles (BEVs), including electric vehicles (EVs) and hybrid electric vehicles (HEVs), have been expected to be an effective mobility option to reduce energy consumption and CO_2

emissions in the transportation sector, it's reasonable to assume that a considerable share of electricity consumption would end up meeting mobility needs, while natural gas is playing an increasingly important role in the electricity mix.

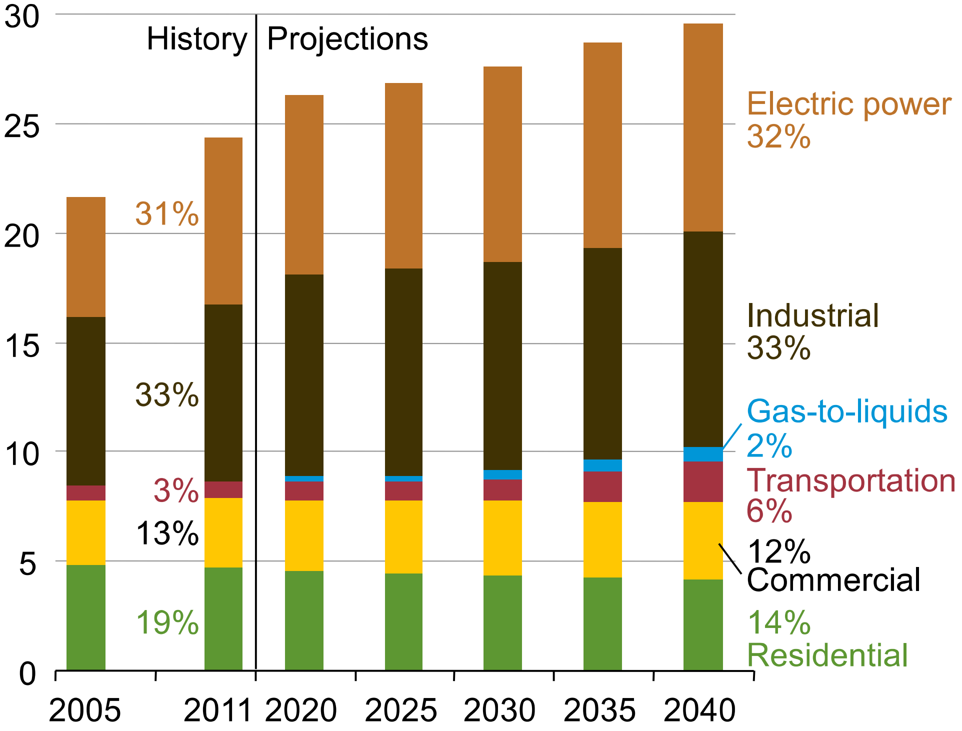

Figure 1-3. U.S. dry natural gas consumption (tcf) by sector, 2005-2040 (Source: EIA)

Vehicle with fuel cells, especially Proton Exchange Membrane Fuel Cell (PEMFC) powered by hydrogen derived from natural gas, although not a noteworthy component in the existing transport sector, is potentially a major player in future transportation, as they promise a more efficient and cleaner mode of mobility. In light of current research and development effort on FCV, it is very likely to become one important part of the natural gas-powered fleets.

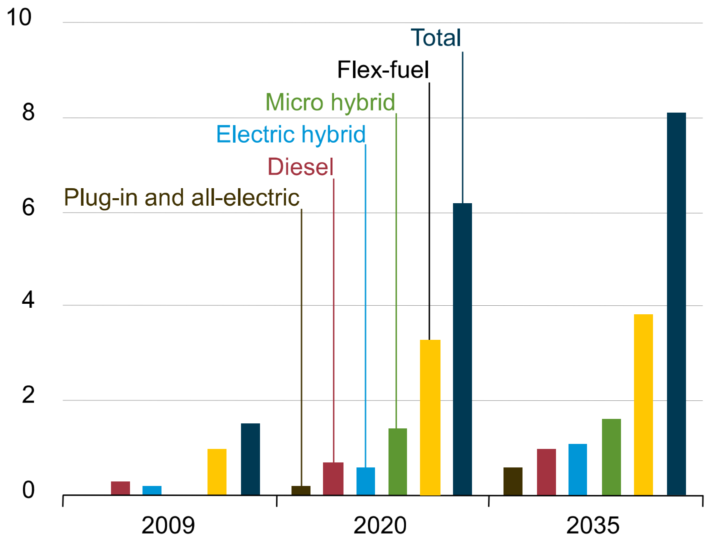

Figure 1-4. U.S. Sales (Million Vehicles Sold) of Unconventional Light-duty Vehicles by Fuel Type, 2009, 2020 and 2035 (Source: EIA)

CNGVs are considered to be a crucial alternative to conventional vehicles in South American and Asian countries, mainly because they have their own natural gas resources to rely on. Contradictory to BEVs, CNGVs in Europe and the U.S. currently play a minor role in the transportation sector, since most of these countries currently or used to depend on imported natural gas. Nevertheless, the study by Engerer and Horn (2010)[3] argued that the promotion of market penetration of natural gas as fuel should be encouraged, especially for conventional engines, considering the necessity to reduce air pollution in big cities[3]. This conclusion is even more applicable to the U.S., as environmental concerns, the increase in natural gas production and the decrease in natural gas price all serve as motives for the switch from petroleum-based vehicles to CNGVs.

Vehicles typically consist of drivetrain, glider and the power source. For the three vehicles under consideration, the major difference in vehicle specification exists in the power source, while the drivetrain and the glider for all the three vehicles are supposed to be similar, if not identical.

For BEVs, the power source is the lithium ion battery (LIB) pack, which can be further broken down into LIB cells, steel box, cables and wiring board[4]. Furthermore, one individual LIB cell possesses many different components, including cathode, anode, electrolyte, separator and casing[4]. Infrastructure with regard to BEV includes a natural gas combined cycle (NGCC) plant[5], electricity transmission and distribution network.

The energy source for CNG vehicles is the internal combustion engine (ICE). Also, a natural gas pressure tank needs to be added as part of the power source[6]. The infrastructure relevant to CNG is represented by distribution networks and fueling stations with onsite compression of natural gas.

The power source for fuel cell vehicles is the fuel cell[7], and the infrastructure pertinent to fuel cell vehicle is represented by a chemical plant capable of converting natural gas into hydrogen[8], distribution networks and fueling stations. Currently, natural gas is generally converted into hydrogen via the steam methane reforming process.

1.3 Life Cycle Assessment

Combining booming of natural gas and changes in transport fleets, it’s almost certain that the use of natural gas and its derivatives for mobility needs would dramatically increase in the coming decades, and the environmental impacts associated with the delivery of driven vehicle miles are worth investigating for the alternative modes of natural gas utilization in the transportation sector.

Life Cycle Assessment (LCA) fits well with this mission. LCA is a technique used to assess the environmental impacts of a product over its life cycle. It can be applied to analyze the contribution of each life cycle stages of a product to the total environmental load, and therefore enables identification of environmental hotspot and provides opportunities of process improvement and optimization of either the product or a specific life cycle stage of the product. In addition, it can be employed to compare between products or product life-cycle stages for internal or external communications. In recent years, LCA becomes popular in environmental policymaking, green manufacturing and eco-design. A typical LCA usually consists of four phases as depicted in Figure 1-5.

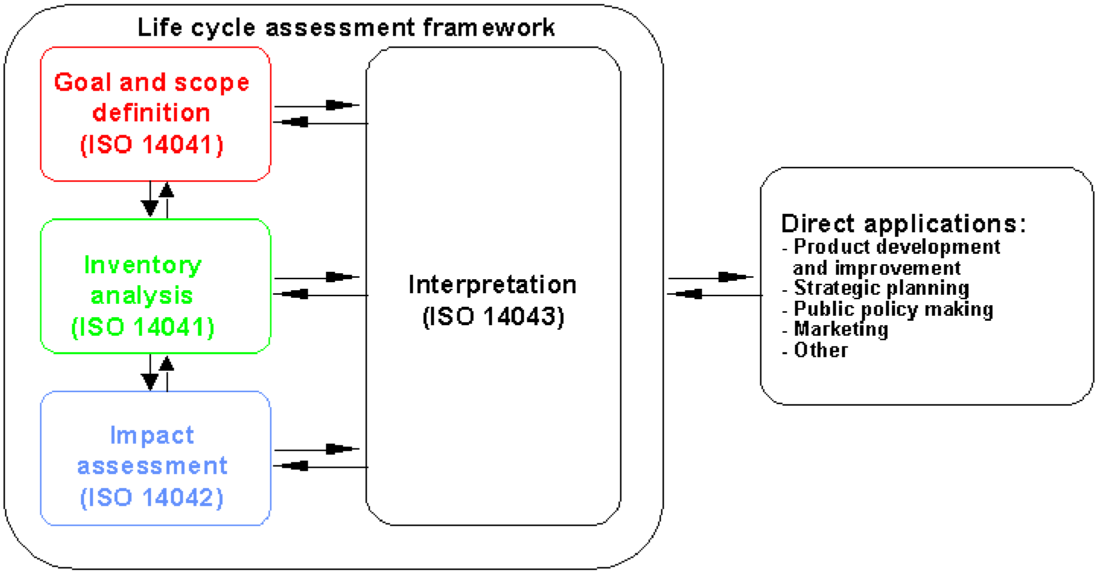

Figure 1-5. Phases of an LCA (International Organization for Standardization (ISO) 2006a)

In the first phase of goal and scope definition, the goal of study is expressed in terms of questions the study wishes to answer, target audience and intended application; the scope of study is described by temporal, geographical and technological coverage of the study, as well as to what extend details of analysis should be included into the study in relation to predefined goal. In the end, objects of study are specified by function, and functional unit is defined as the basis for comparison of different products of product stages.

The second phase, Life Cycle Inventory (LCI) defines the product system by constructing a model of environmental inflows and outflows. To be specific, after setting system boundary and cutoff criteria, unit processes involved in the LCA study are defined and expressed in the flow diagram of the product. Then data for each of the unit processes is collected, including material and energy inputs to each unit process, as well as emissions from each process. Collected data are eventually summarized in a table listing quantified inputs and outputs associated with the environment resulted from the function unit.

In the third phase of Life Cycle Impact Assessment (LCIA), the results of LCI are processed and interpreted as impacts to the environment. To be specific, a list of impact categories is firstly defined, then environmental models are selected to relate the entries in the LCI table to relevant changes and interventions to the environment, which can be further linked to the selected impact categories, also known as midpoints indicators. Thereafter, an optional normalization step can be carried out to calculate the share of each midpoint indicator to the total impacts worldwide or regional. By grouping midpoint indicators representing the same environmental concern, one can derive endpoint indicators, whose values are calculated by summing up the normalized value midpoint indicators in the same group. In the end, an optional weighting step can be adopted to include perceptions of relative importance of different endpoint indicators.

The fourth phase, interpretation evaluates the soundness of the results against the choices and assumptions made during the entire analysis. It mainly includes evaluation of results in terms of consistency and completeness, analysis of results in terms of robustness and the articulation of conclusions and recommendations generated by the study.

1.4 Existing Research and Knowledge Gaps

As a tool capable of evaluating the environmental friendliness of a product and thereby aiding in ecological design, Life Cycle Assessment (LCA) has been applied to several personal transportation options, especially electric vehicles and hybrid electric vehicles with batteries.

From 2004 and 2005, the Sustainable Batteries (SUBAT) project[9] was carried out in the Netherlands to identify the most environment-benign battery intended for electric and hybrid electric vehicles, and to examine the possibility to allow the extended use of nickel-cadmium traction batteries in electric vehicles beyond 2005. In the project, five commercially available or soon-to-be available batteries were considered, including lead-acid, nickel-cadmium, nickel-metal hydride, lithium-ion based on a $LiCoO_2$ cathode, and sodium-nickel chloride batteries. Each of the five batteries was thoroughly studied from technical, environmental and economic perspectives respectively. The environmental assessment was basically a life cycle assessment of the five batteries using a “cradle to grave” approach. The modeling was done in SimaPro 6.01, and the environmental impacts were expressed in a score using the Ecoindicator 99 method with a hierarchist perspective. The results indicate that lithium-ion and sodium-nickel chloride batteries have the lowest environmental impacts. It’s also claimed that the manufacturing phase and use phase are comparable in magnitude of environmental impacts, since recycling of waste materials significantly compensates for the environmental impacts from the manufacturing phase. However, it should be noted that the conclusion was based on an ideal recycling rate as high as 95%, which is not quite practical given the current status of battery recycling technology. A sensitive analysis was also included in the project, justifying that the result is independent of assumptions concerning battery composition and energy consumption.

Following the track of the SUBAT project, Zackrisson *et al* (2010)[10] applied LCA to batteries for plug-in hybrid electric vehicles (PHEVs). They studied two lithium-ion batteries based on a $LiFePO_4$ cathode with different solvents for electrolytes. A "cradle to grave" approach was also adopted, only that the recycling phase was simply represented by transportation of waste materials due to lack in information on $LiFePO_4$ recycling. The environment impacts were represented by five impact categories including global warming, acidification, ozone depletion, photochemical smog and eutrophication. Materials and energy inputs were mainly taken from the Ecoinvent 2.0 database, and modeling was also done in SimaPro. The results confirmed the conclusion of the SUBAT project that the environmental impacts of the use phase, ranging from 17% to 50%, are in the same order of magnitude compared to that of the production phase. It's also pointed out that battery efficiency is more important than battery weight when looking at the environmental impacts of the use phase. As for the two different solvents for electrolytes, they argued that water is more environmental friendly than N-methyl-2-pyrrolidone (NMP), with more than 20% reduction in life-cycle global warming potential. The robustness of results was also tested by recalculations using extreme yet practical data of battery efficiency, electricity mix and the relationship between weight and energy of PHEV.

Another study on the life cycle environmental assessment of lithium-ion and NiMH batteries for PHEVs and battery electric vehicles (BEVs) was published by Majeau-Bettez *et al* (2011)[11] recently. They were especially interested in nickel cobalt manganese (NCM) and LFP as cathode materials for lithium-ion batteries. After constructing a component-wise life cycle inventory for the batteries and evaluating the environmental impacts using midpoint indicators, they found that on a per-storage basis, NiMH based batteries have the highest environmental impacts, followed by those based on NCM and LFP consecutively. They attributed the environmental benefits of LFP to less environmentally intensive materials use at the manufacturing phase, as well as greater lifetime expectancy, which is responsible for reductions of environmental impacts during the use phase. In their study, they acknowledged the importance of energy requirements during the manufacturing phase as a major cause of global warming potential. They also pointed out the dominance of nickel in the environmental impacts of the battery pack, in categories include but are not limited to ecotoxicity, acidification potential and abiotic depletion potential. During the sensitivity analysis, they suggested that assumptions of battery efficiency and life expectancy appear to be of high uncertainties, as a result of scarce data on real-world performance of batteries used on PHEVs and BEVs.

Besides interests in the differences of batteries alone, efforts have also been made to assess environmental impacts of battery-powered electric vehicles (BEVs) and internal combustion engine vehicles (ICEVs). Notter *et al* (2010)[12] looked at a BEV powered by a

$LiMn_2O_4$ cathode based battery and compared it against a similar ICEV. End-of-life (EOL) was also modeled in the study, except that recycling of materials was not assumed to offset the environmental burdens caused by the production phase. Ecoinvent 2.0 and SimaPro were again employed in this LCA application. The environmental impact categories were chosen to be global warming potential, cumulative energy demand, abiotic depletion potential and the Ecoindicator 99 with the hierarchist perspective and average weighting. It's concluded from the study that the use phase accounted for 45.9% to 63.5% of the total impacts across different categories and therefore is the largest contributor to the environmental burden of both BEV and ICEV. The divergence of this conclusion from that of other studies is due to the differences in the definition of functional unit. Notter *et al* also found that copper used as collector foil in anode, which is responsible for as high as 43% of environmental burdens from the production phase, is a hot spot in the production phase. They also pointed out the importance of metal supply and process energy in the assessment of environmental impacts resulted from the production phase. In the sensitivity analysis, it's revealed that this analysis is slightly sensitive to assumptions on cathode chemistry and vehicle lifespan, while the sensitivity to assumptions on electricity mix is moderate.

Ma *et al* (2012)[13] examined the life cycle greenhouse gas (GHG) emissions of BEVs which are to be introduced to the UK and California market in 2015 and contrasted the results to that of an ICEV. They reinforced that the life cycle GHG emissions are lower than that of ICEV, while the emission associated with the vehicle manufacturing for BEV is higher. They also pointed out that driving conditions and the marginal environmental impacts with regard to additional electricity requirement by BEVs were important factors when evaluating the life cycle impacts of BEVs.

The effect of BEV use profile on its life cycle assessment was addressed in another study by Faria et al (2013)[14]. They also found that the life cycle GHG emissions and energy consumptions of BEVs were very sensitive to driving profiles, and aggressive driving behaviors could increase the total energy consumptions up to 50%. They also investigated the importance of electricity mix. They concluded that although BEVs were sustainable from an environmental perspective, they could be made better by charging from a greener electricity mix and being driven with a more eco-concerned attitude.

Besides reducing GHG emissions and other environmental impacts, BEVs are also expected to offer benefits to the energy system. In a recent study by Richardson (2013)[15], BEVs were found to be able to significantly reduce the renewable energy over-generated in an electric system and therefore could serve as a viable option to help renewable energy integration into the electric grid.

As part of the infrastructure for natural gas-powered BEVs, a power plant fired by natural gas should be included in the LCA study. National Renewable Energy Laboratory (NREL) carried out an LCA study of natural gas combined-cycle (NGCC) power generation system in 2000[16]. Construction of power plant and natural gas infrastructure, production and distribution of natural gas, removal of NO_x by selective catalytic reduction, as well as power plant operation were considered in the analysis. It's concluded that natural gas production and distribution was the single largest contributor in terms of energy demand, resource depletion, water pollution, and solid waste, while operation of the power plant accounted for most of the CO_2 emissions. The study also presented power plant efficiency and natural gas loss as two crucial parameters exerting the largest effect on the results.

Raugei *et al* (2005)[17] did an LCA comparison of Molten Carbonate Fuel Cells (MCFC) and natural gas turbines employed in natural gas-fired power plants. Three types of natural gas power plants are investigated, including semi-closed gas turbine combined cycle, NGCC and steam turbine and gas turbine cogeneration plant. The material/exergy flows and airborne emissions are well documented for each type of power plants. The results indicate that NGCC plant is superior to its alternatives in terms of abiotic intensity, water intensity, LCA energy efficiency and CO_2 intensity.

In addition to the power plant, the charging infrastructure for BEVs was also investigated by LCA practitioners. Lucas *et al* (2012)[18] looked into the environmental impacts associated with the charging point's network for BEVs and compared it against the impacts resulted from the infrastructure of ICEVs. They found that although the carbon and energy intensity of BEV charging infrastructure were about six times as high as that of ICEV infrastructure, when comparing with the total life cycle impacts, its contribution was less than 8% and was not significant.

LCA studies on CNG vehicles haven't got much academic interest. One LCA analysis on natural gas vehicles that has been found in the literature review is done by Ally and Pryor (2007)[19]. As part of the Sustainable Transport Energy Program (STEP) initiated by the Government of Western Australia, they did an LCA comparison of bus fleets powered by diesel, natural gas and hydrogen fuel cell respectively. Overall environmental impacts and cumulative energy demand are investigated for all life cycle stages of the transportation system, including infrastructure, bus manufacturing and operation, as well as end-of-life. Specifically, the natural gas infrastructure is represented by fuelling stations taken from GaBi database, pipeline transportation and electrically powered gas compressors. It's concluded that bus burning natural gas is superior to its counterparts when looking at acidification potential and photochemical ozone creation potential. It also gives better environmental footprints with regard to primary energy demand compared with the fuel cell vehicle, winning over diesel vehicle in terms of eutrophication potential, while receiving the last place when it comes to the impact category of global warming potential.

Rose *et al* (2013)[20] carried out a comparative LCA on refuse collection vehicles powered by diesel and compressed natural gas (CNG) respectively. They concluded that the switch to a CNG-based fleet would offer life cycle GHG emissions, mostly due to less CO_2 emissions from feedstock production, fuel production and vehicle operation. Considerable cost savings and marginal energy savings could be also realized through the switch.

Fuel cell vehicles are also a potential major player in future transportation, as they promise a more efficient and cleaner alternative of mobility[21]. As part of the effort to realize U.S. energy independence, the Freedom Cooperative Automotive Research (CAR) program was initiated[22]. Through the partnership between Department of Energy (DOE) and major automobile manufacturers in the U.S., this program aims to promote the development of fuel cell operating systems for cars and trucks. Under the support of

DOE, extensive Research and Development efforts have been exerted on fuel cell vehicles, and the environmental impacts of fuel cell vehicles have attracted the attention of LCA practitioners.

Granovskii *et al* (2006)[23] did an LCA comparison of hydrogen and gasoline vehicles. The hydrogen vehicle studied in the analysis utilized a PEMFC, with natural gas as the feedstock of hydrogen. Life cycle stages considered for the hydrogen vehicles included natural gas pipeline transportation, natural gas reforming, hydrogen compression and distribution, as well as the use phase of the vehicles. The results of the comparison indicated that a hydrogen fuel cell vehicle was competitive compared with a gasoline one, with a 25% to 30% higher efficiency, and therefore sizable reduction in energy depletion and GHGs emissions.

The environmental soundness of PEMFC powered automobiles was further justified in the LCA study done by *Hussain* et al (2007)[24]. In this analysis, the manufacturing of vehicles was also considered, in addition to the manufacturing and distribution of fuel, as well as the operation of the vehicle. Based on the comparison, a PEMFC vehicle consumed 2.3 times less energy than an ICE vehicle, and correspondingly resulted in GHGs emissions that were 2.6 times lower than an ICE vehicle. This study also pointed out fuel production as the major contributor to both energy depletion and GHGs emission in the fuel cycles. In the vehicle cycles, use phase accounted for more than 80% of both the total energy depletion and GHGs emissions for the ICE vehicle, while the manufacturing phase dominated the total life cycle GHGs emissions for the PEMFC vehicle.

As both the BEVs and FCVs are promising future transportation alternatives, a few life cycle studies have been carried out to compare the environmental footprint of BEVs and FCVs. Wang *et al* (2013)[25] examined the environmental outlook of BEVs and FCVs in China. They found that BEVs were not suitable for deployment in China, as China relies heavily on coal for electricity generation at present. FCVs, on the other hand, if powered by hydrogen produced from natural gas reforming, could achieve energy conservation and GHG reduction relative to BEVs and ICEVs.

Hwang *et al* (2013)[26] compared the environmental performances of BEVs and FCVs based on U.S. data. The conclusion was that, when charged by electricity from the U.S. grid, which was also dominated by fossil fuels, BEVs resulted in a life cycle energy consumption that was 30% higher than that of FCVs burning hydrogen reformed from natural gas, and a total GHG emissions that was 50% higher than that of the FCVs.

Garcia Sanchez *et al* (2013)[27] investigated the life cycle comparison of bus fleets powered by diesel, electricity and hydrogen in Spain, where 50% of the electricity comes from natural gas. They pointed out that given the electricity mix of Spain, electric buses would be the most environmental benign fleets, in terms of both total energy consumption and life cycle GHG emissions. The environmental performances of hydrogen powered buses, however, were not optimistic due to a fuel economy that was more than two times as large as that of the electric buses.

Being the infrastructure component of the system for fuel cell vehicles, the natural gas reforming plant has also been studied from an LCA perspective. In 2001, NREL completed an LCA of a hydrogen production plant via steam reforming of natural gas[28], focusing on processes required to transform natural gas into hydrogen, in addition to natural gas production and distribution. The results revealed that plant operation accounted for 75% of the GWP. Plant operation was also hold responsible as the largest contributor to total energy consumption, while the majority of waste was generated in the processes pertaining to natural gas production and distribution. The study also indicated that the system was relatively sensitive to the assumption on the energy efficiency of the plant. Assumptions on the natural gas losses at the plant also had noticeable impact with regard to GWP and total energy consumption.

These studies all promote the use of natural gas in the transportation sector from an environmental perspective. However, a direct comparison between the environmental impacts of different natural-gas powered vehicles reported in the aforementioned literature is not feasible, due to differences in definition of functional unit and system boundaries adopted in these analyses. Therefore, a life cycle comparison based on the same functional unit and system boundary for different natural gas-powered mobility alternatives is crucial to our understanding of the environmental consequences from the transition of energy resources from coal and petroleum to natural gas.

The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET) developed and maintained by Argonne National Laboratory[29] provides life cycle GHG emissions, energy consumptions and criteria air pollutants emissions for a wide range of light-duty vehicles based on multiple fuel conversion pathways. It examines the respective burdens associated with the well to pump process, the vehicle cycle and the vehicle operation and can offer some insight into the environmental friendliness of natural gas-based personal mobility alternatives. However, the GREET model has its own limitations. Firstly, the GREET model only contains energy consumptions and criteria air pollutants emissions in its inventory for all of the processes it modeled. This is sufficient for the calculation of life cycle global warming potential and cumulative energy demand, but is inadequate for calculations for impact categories related to human health and ecosystem quality, where water emissions and other air pollutants emissions, especially those of copper, lead and arsenic, can significantly affect the results.[9] Secondly, the GREET model does not consider water flows in the life cycle of the vehicles. This makes it impossible to evaluate water footprint, which is currently one of the hot topics in life cycle modeling. Thirdly, the GREET model does not examine the vehicle cycle and the fuel-to-well conversion for BEV and FCV in depth. For BEV, it only models the $LiMn_2O_4$ cathode chemistry and does not consider the effect of the electrochemical properties of the LIB on the life cycle performances of BEV. For FCV, a detailed inventory for the fuel cell stack is not reported. The incompleteness of the life cycle inventory and the simplification in the use phase modeling make it problematic to realistically evaluate the environmental impacts pertaining to the assembly of the power source and the use phase of BEV and FCV, and therefore could not provide satisfactory answers to the overarching question of this study. Last but not least, the data structure of the GREET model does not allow the user to track down the contribution of a single process or a single material or energy input to the total life cycle impacts and therefore pose difficulty in pinpointing the environmental hot spots and identifying opportunities of impact reduction.

To fill these knowledge gaps, a systematic and detailed life cycle comparison needs to be made for different personal transportation modes powered by natural gas. In addition, environmental hotspots pertaining to each of the three transportation options need to be further examined. For BEVs, little attention has been paid to impacts of LIB component material choices on the total environmental burden of BEVs. Since different materials of components can result in differences in power, energy density and cycling performance of batteries and therefore affect the use phase environmental burdens of BEVs, in this analysis different cathode chemistries, anode chemistries and electrolytes that are commercially available for LIBs are considered. Because the use of organic solvents and process heat associated with different synthesis methods are supposed to cause significant differences in environmental impacts pertaining to the production phase, different pathways of synthesis of cathode materials were also investigated in this study. It's expected that the LCA study on BEVs could provide insights from a life-cycle perspective into possible improvement of battery technology for BEVs in terms of cathode, anode and electrolyte materials manufacturing.

For CNG vehicles, a complete LCI is nonexistent in current literature, probably due to the minimal presence of CNG vehicles in the market of Europe and the U.S.. In this research, LCI for CNGV is constructed based on LCI of internal combustion engine vehicles[11], specifications of CNG infrastructure[13, 30] and fuel efficiency and performance of CNG[31-32].

For FCVs, the challenge is more significant. FCVs are still under rigorous development, with limited applications on light traction vehicles and scooters. The lack of data on FCVs poses great difficulty to the construction of LCI, that's probably why LCI of

PEMFC is not reported in any of the existing LCA studies. Moreover, the performances of FCVs as passenger vehicles remain largely unknown, suggesting another difficulty in modeling the use phase of FCVs. In this analysis, LCI for FCV is put together based on best available data found in literature[33-34], with high uncertainty assigned to key technology parameters to test the sensitivity of LCA results to different assumptions.

Adding carbon capture and sequestration (CCS) to a power or chemical plant has great potential to reduce GHG emissions. Among the three natural gas-based mobility modes, CNG vehicles may be competitive in terms of the relatively simple infrastructure required. However, if environmental impact is more of the concern, BEVs and fuel cell vehicles may be more promising, since CCS technology can be applied to the NGCC power plant and the steam reforming chemical plant to avoid extensive CO_2 emissions[4, 8]. On the other hand, the addition of CCS unit may cause marginal increase in capital cost, water consumption and land use. Nonetheless, none of current LCA studies on natural gas-powered vehicles included CCS in their system boundaries. Therefore, in this study a scenario analysis of CCS addition to the NGCC plant and the SMR plant is implemented, with the goal to study the trade-off between the economic benefit of CNG vehicles and the environmental benefit of BEVs and FCVs.

Problems and limitations associated with LCA are also one of the key topics of LCA research. Being unable to address spatial and temporal variations has long been known as one of the major limitations of LCA studies[35-36]. Among the several research efforts[37-45] attempting to fill this gap, geoinformation system is embedded in LCA to account for spatial variations, and temporal variations is generally addressed by applying a discounting rate to the material and energy flow to reflect technological improvement. The discounting method, although convenient, contradicts with the fact that technology evolves at different paces for technologies at different diffusion stages. The object of this study, light-duty passenger vehicle, is a product of long lives, which is likely to be subjected to the uncertainty inherent with future events, as continuous advances towards cleaner power generation and transportation technology are expected in the next few decade. In this dissertation study, performance curve model[46] is adopted to forecast technological progression rates for the three natural gas-based transportation technologies. Future environmental legislation is also incorporated into the LCA study to better examine the effect of temporal variation.

LCA is also well known for its inherent uncertainties due to ecosphere and external uncertainties because of materials and energy inputs in the technosphere[47]. Stochastic modeling, especially Monte Carlo simulation with random samplings, and scenario analysis is used to estimate uncertainty propagation in this analysis.

1.5 Goal of Study and Structure of Dissertation

The overarching goal of this dissertation study is to investigate the environmental benefits and costs associated with different natural gas-based mobility options. A complete and dependable LCI of the system is the premise of a plausible LCA study. Therefore, the first task is collecting data constituting LCI of the systems from reliable sources. For data gaps, valid assumptions are made, and caution is taken to examine the sensitivity of LCA results to these assumptions. The second task is to compare the environmental impacts across different impact categories for the three natural gas-based mobility modes. After carrying out life cycle impact assessment of the three vehicles, we present some insight into the most environmentally favorable mode of personal transportation powered by natural gas. On the other hand, it's understood that environmental concern alone doesn’t necessarily shape future transportation. Therefore, we also identify environmental hotspots and provide suggestions on how to reduce the environmental burdens of each mode. For current vehicles, future technology advances and environmental legislations are very likely to mitigate the environmental impacts evaluated at present. The third task then is to provide a novel solution to the uncertainty and temporal variability inherent with future technology advance, and thereby make the LCA results representing the status quo meaningful in a technology-evolving context.

This dissertation consists of six chapters, this introductory chapter followed by chapters 2-6, among which Chapters 2-5 are the results-based chapters, and chapter 6 serves as the summary. In chapter 2, environmental impacts associated with the manufacturing of different LIB component materials that are commercially available are examined. Two synthesis methods for cathode active materials, calcination and sol-gel, are also investigated as an effort to evaluate the environmental burden attributed to process heat input and organic solvent use in the manufacturing process. Chapter 3 focuses on the use phase of BEVs, with a special emphasis on electrochemical properties of different active cathode materials and their impact on the life cycle environmental performance of BEVs. Chapter 4 compares the environmental friendliness of the three natural gas-powered passenger vehicles, examines the cost and benefit of CCS technologies, and identifies opportunities to reduce environmental footprint. Chapter 5 applies Wright’s law to key technology parameters relevant to the three mobility modes to study temporal variations resulted from technological progression, and constructs scenarios to account for possible changes to LCIs due to future environmental policy enforcement. For all of the four chapters, Monte Carlo simulation is performed to account for uncertainties pertaining to each LCA study and test the robustness of the results to assumptions.

References

[1]. *Annual Energy Outlook 2011 Reference Case.* U.S. Department of Energy, U.S. Energy Information Administration, Office of Integrated and International Energy Analysis, Washington, DC, U.S., 2011.

[2]. *Annual Energy Outlook 2013 with Projections to 2040.* U.S. Department of Energy, U.S. Energy Information Administration, Office of Integrated and International Energy Analysis, Washington, 2013; http://www.eia.gov/forecasts/aeo/pdf/0383(2013).pdf

[3]. Engerer, H.; Horn, M. Natural gas vehicles: an option for Europe. *Energ. Policy.* 2010, 38, 1017-1029.

[4]. Ozawa, K., Eds. *Lithium Ion Rechargeable Batteries: Materials, Technology, and New Applications*. WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2009.

[5]. *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*; National Energy Technology Laboratory: Golden, CO, 2010: http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf

[6]. Collantes, G.; Melaina, M.W. The co-evolution of alternative fuel infrastructure and vehicles: a study of the experience of Argentina with compressed natural gas. *Energ. Policy.* 2011, 39, 664-675.

[7]. Hordeski, M.F. *Hydrogen & Fuel Cells: Advances in Transportation and Power.* The Fairmont Press, Inc.: Lilburn, GA, 2009.

[8]. *HTGR-Integrated Hydrogen Production via Steam Methane Reforming (SMR) Process Analysis;* Idaho National Laboratory: Idaho Falls, ID, 2010; https://inlportal.inl.gov/portal/server.pt/document/78381/htgr-integrated_hydrogen_production_via_steam_methane_reforming_-smr-_economic_analysis_pdf

[9]. Van Den Bossche, P.; Vergels, F.; Van Mierlo, J.; Matheys, J.; Van Autenboer, W. SUBAT: An assessment of sustainable battery technology. *J. Power Sources.* 2006, 162, 913–919.

[10]. Zackrisson, M.; Avellan, L.; Orlenius, J. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles---critical issues. *J. Cleaner Production.* 2010, 18, 1519-1529.

[11]. Majeau-Bettez, G.; Hawkins, T.R.; Stromman, A.H. Lief cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. *Environ. Sci. Technol.* 2011, 45, 4548-4554.

[12]. Notter, D. A.; Gauch, M.; Widmer, R.; Wager, P.; Stamp, A.; Zah, R.; Althaus, H.-J. Contribution of Li-ion batteries to the environmental impact of electric vehicles. *Environ. Sci. Technol.* 2010, 44, 6550–6.

[13]. Ma, H.R,; Balthasar, F.; Tait, N. A new comparison between the life cycle greenhouse gas emissions of battery electric vehicles and internal combustion vehicles. *Energ. Policy*. 2012, 44, 160-173.

[14]. Faria, R.; Marques, P.; Moura, P. Impact of the electricity mix and use profile in the life-cycle assessment of electric vehicles. *Renewable Sustainable Energy Reviews.* 2013, 24, 271-287.

[15]. Richardson, D.B. Electric vehicles and the electric grid: a review of modeling approaches, impacts and renewable energy integration. *Renewable Sustainable Energy Reviews.* 2013, 19, 247-254.
[16]. *Life Cycle Assessment of a Natural Gas Combined-Cycle Power Generation System.* U.S. Department of Energy, National Renewable Energy Laboratory, Golden, CO, U.S., 2000.
[17]. Raugei, M.; Bargigli, S.; Ulgiati, S. A multi-criteria life cycle assessment of molten carbonate fuel cells (MCFC) --- a comparison to natural gas turbines. *Int. J. Hydrogen Energ.* 2005, 30, 123-130.
[18]. Lucas, A.; Silva, C.A.; Neto R.C. Life cycle analysis of energy supply infrastructure for conventional and electric vehicles. *Energ. Policy.* 2012, 41, 537-547.
[19]. Ally, J.; Pryor, T. Life-cycle assessment of diesel, natural gas and hydrogen fuel cell bus transportation systems. *J. Power. Sources.* 2007, 170, 401-411.
[20]. Rose, L.; Hussain, M.; Ahmed, S. A comparative life cycle assessment of diesel and compressed natural gas powered refuse collection vehicles in a Canadian city. *Energ. Policy.* 2013, 52, 453-461.
[21]. *Alternatives to Traditional Transportation Fuels 2009.* U.S. Department of Energy, U.S. Energy Information Administration, Office of Integrated and International Energy Analysis, Washington, DC, U.S., 2011.
[22]. Hordeski, M.F. *Hydrogen & Fuel Cells: Advances in Transportation and Power.* The Fairmont Press, Inc.: Lilburn, GA, 2009.
[23]. Granovskii, M.; Dincer, I.; Rosen, M.A. Life cycle assessment of hydrogen fuel cell and gasoline vehicles. *Int. J. Hydrogen Energy.* 2006, 31, 337-352.
[24]. Hussain, M.M.; Dincer, I.; Li, X. A preliminary life cycle assessment of PEM fuel cell powered automobiles. *Applied Thermal Eng.* 2007, 27, 2294-2299.
[25]. Wang, D.W.; Zamel, N.; Jiao, K.; Zhou, Y.B. Life cycle analysis of internal combustion engine, electric and fuel cell vehicles for China. *Energy.* 2013, 59, 402-412.
[26]. Hwang, J.J.; Kuo, J.K.; Wu, W. Lifecycle performance assessment of fuel cell/battery electric vehicles. *Int. J. Hydrogen Energ.* 2013, 38, 3433-3446.
[27]. Garcia Sanchez, J.A.; Martinez, J. M. L.; Martin, J. L. Impact of Spanish electricity mix, over the period 2008-2030, on the life cycle energy consumption and GHG emissions of electric, hybrid diesel-electric, fuel cell hybrid and diesel bus of the mardrid transportation system. *Energ. Conversion Manag.* 2013, 74, 332-343.
[28]. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming.* . U.S. Department of Energy, National Renewable Energy Laboratory, Golden, CO, U.S., 2001.
[29]. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model, Argonne National Laboratory;
https://greet.es.anl.gov/
[30]. Nigge, K.-M. *Life Cycle Assessment of Natural Gas Vehicles: Development and Application of Site-dependent Impact Indicators*; Springer: Berlin, Germany, 2000.
[31]. Annual Certification Test Results & Data, United States Environmental Protection Agency;
http://www.epa.gov/otaq/crttst.htm
[32]. Test Car List Data Files, United States Environmental Protection Agency;
http://www.epa.gov/otaq/tcldata.htm

[33]. *Cost Analysis of PEM Fuel Cell Systems for Transportation;* TIAX LLC: Cambridge, MA, 2005; http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/tiax_fc_cost_analysis_2005.pdf

[34]. *National Fuel Cell Electric Vehicle Learning Demonstration Final Report;* National Renewable Energy Laboratory: Golden, CO, 2012; http://www.nrel.gov/hydrogen/pdfs/54860.pdf

[35]. Reap, J.; Roman, F.; Duncan, S.; Bras, B. A survey of unresolved problems in life cycle assessment. Part 1: goal and scope and inventory analysis. *Int. J. Life Cycle Assess.* 2008, 13, 290-230.

[36]. Reap, J.; Roman, F.; Duncan, S.; Bras, B. A survey of unresolved problems in life cycle assessment. Part 2: impact assessment and interpretation. *Int. J. Life Cycle Assess.* 2008, 13, 374-388.

[37]. Azevedo, L.B.; Henderson, A.D.; Van Zelm, R.; Jolliet, O.; Huijbregts, M.A.J. Assessing the importance of spatial variability versus model choices in life cycle assessment: the case of freshwater eutrophication in Europe. *Environ. Sci. Technol*. 2013, 47, 13565-13570.

[38]. Dresen, B.; Jandewerth, M. Integration of spatial analyses into LCA – calculating GHG emissions with geoinformation systems. *Int. J. Life Cycle Assess.*2012, 19, 1094-1103.

[39]. Gasol, C.M.; Gabarrell, X.; Rigola, M. Gonzalez-Garcia, S.; Rieradevall, J. Environmental assessment: (LCA) and spatial modelling (GIS) of energy crop implementation on local scale. *Biomass Bioenerg.* 2011, 35, 2975-2985.

[40]. Kendall, A. Time-adjusted global warming potentials for LCA and carbon footprints. *Int. J. Life Cycle Assess.*2012, 17, 1042-1049.

[41]. Levasseur, A.; Lesage, P.; Margni, M.; Deschenes, L.; Samson, R. Considering time in LCA: dynamic LCA and its application to global warming impact assessment. *Environ. Sci. Technol*. 2010, 44, 3169-3174.

[42]. Stasinopoulos, P.; Compston, P.; Newell, B.; Jones, H.M. A system dynamics approach in LCA to account for temporal effects – a consequential energy LCI of car body-in-whites. *Int. J. Life Cycle Assess.* 2012, 17, 199-207.

[43]. Yuan, C.Y.; Simon, R.; Mady, N.; Dornfeld, D. Embedded temporal difference in life cycle assessment: case study on VW Golf A4 car. Proceedings of IEEE International Symposium on Sustainable Systems and Technology, Phoenix, AZ, May 18-20, 2009.

[44]. McNerney, J.; Farmer, J.D.; Redner, S.; Trancik, J.E. Role of design complexity in technology improvement. *P. Natl. Acad. Sci. USA.* 2011, 108, 9008-9013.

[45]. Lloyd, S.M.; Ries, R. Characterizing, propagating, and analyzing uncertainty in life-cycle assessment. *J. Ind. Ecol*. 2007, 11, 161-179.

Chapter 2.

LCA Study of Lithium-ion Battery: Manufacturing Phase

2.1 Introduction

As a tool capable of evaluating the environmental friendliness of a product and thereby aiding in ecological design, Life Cycle Assessment (LCA) in recent years has been applied to several products providing energy storage, especially batteries used in electric vehicles and hybrid electric vehicles.

From 2004 and 2005, the Sustainable Batteries (SUBAT) project was carried out in Netherland to identify the most environment-benign battery intended for electric and hybrid electric vehicles, and to examine the possibility to allow the extended use of nickel-cadmium traction batteries in electric vehicles beyond 2005[1]. In the project, five commercially available or soon-to-be available batteries were considered, including lead-acid, nickel-cadmium, nickel-metal hydride (NiMH), lithium-ion based on a $LiCoO_2$ cathode, and sodium-nickel chloride batteries. Each of the five batteries was thoroughly studied from technical, environmental and economic perspectives respectively. The results indicate that lithium-ion and sodium-nickel chloride batteries have the lowest environmental impacts evaluated by eco-`indicator points, due to lower environmental burden associated with both the manufacturing phase and the use phase. It's also claimed that the manufacturing phase and use phase are comparable in magnitude of environmental impacts, since recycling of waste materials significantly compensates for the environmental impacts from the manufacturing phase. However, it should be noted that the conclusion was based on an ideal recycling rate as high as 95%, which is not quite practical given the current status of battery recycling technology. A sensitivity analysis was also included in the project, justifying that the result is independent of assumptions concerning battery composition and energy consumption.

Following the track of the SUBAT project, Zackrisson *et al* applied LCA to batteries for plug-in hybrid electric vehicles (PHEVs) [2]. They studied two lithium-ion batteries based on a $LiFePO_4$ (LFP) cathode with different solvents for electrolytes. The results confirmed the conclusion of the SUBAT project [1] that the environmental impacts of the use phase, ranging from 17% to 50%, are in the same order of magnitude compared to that of the production phase. It's also pointed out that battery efficiency is more important than battery weight when looking at the environmental impacts of the use phase. As for the two different solvents for electrolytes, they argued that water is more environmental friendly than N-methyl-2-pyrrolidone (NMP), with more than 20% reduction in life-cycle global warming potential. The robustness of results was also tested by recalculations using extreme yet practical data of battery efficiency, electricity mix and the relationship between weight and energy of PHEV.

Another study on the life cycle assessment of lithium-ion and NiMH batteries for PHEVs and battery electric vehicles (BEVs) was published by Majeau-Bettez *et al* recently [3].

They were particularly interested in nickel cobalt manganese (NCM) and LFP as cathode materials for lithium-ion batteries. After constructing a component-wise life cycle inventory for the batteries and evaluating the environmental impacts using midpoint indicators, they found that on a per-storage basis, NiMH based batteries have the highest environmental impacts, followed by those based on NCM and LFP consecutively. They attributed the environmental benefits of LFP to less environmentally intensive materials use at the manufacturing phase, as well as greater lifetime expectancy, which is responsible for reductions of environmental impacts during the use phase. In their study, they acknowledged the importance of energy requirements during the manufacturing phase as a major cause of global warming potential. They also pointed out the dominance of nickel in the environmental impacts of the battery pack, in categories include but are not limited to ecotoxicity, acidification potential and abiotic depletion potential. During the sensitivity analysis, they suggested that assumptions of battery efficiency and life expectancy appear to be of high uncertainties, as a result of scarce data on real-world performance of batteries used on PHEVs and BEVs.

Besides interests in the differences of batteries alone, efforts have also been made to assess environmental impacts of BEVs and internal combustion engine vehicles (ICEVs). Notter *et al* looked at a BEV powered by a $LiMn_2O_4$ cathode based battery and compared it against a similar ICEV [4]. End-of-life was also modeled in the study, except that recycling of materials was not assumed to offset the environmental burdens caused by the production phase. It's concluded from the study that the use phase accounted for 45.9%-63.5% of the total impacts across different categories and therefore is the largest contributor to the environmental burden of both BEV and ICEV. The divergence of this conclusion from that of other studies is due to the differences in the definition of functional unit. The SUBAT project used a function unit of a single-charge range of 60 km. Majeau-Bettez *et al* defined the function unit to be 50MJ of energy stored in the battery and delivered to the powertrain, while Notter *et al* chose a function unit of 150,000 km driven. Notter *et al* also found that copper used as collector foil in anode, which is responsible for as high as 43% of environmental burdens from the production phase, is a hot spot in the production phase. They also addressed the importance of metal supply and process energy in the assessment of environmental impacts resulted from the production phase. In the sensitivity analysis, it's revealed that this analysis is slightly sensitive to assumptions on cathode chemistry and vehicle lifespan, while the sensitivity to assumptions on electricity mix is moderate.

The three studies all acknowledged the considerable contribution of the manufacturing phase of LIBs to the overall life cycle environmental impacts of the BEV, and provided recommendations for impact reduction. However, these recommendations were more focused on the manufacturing and assembly processes of the LIB, with limited further examination on the upstream synthesis processes of limited cathode materials. Since each component constituting the LIB can be produced from different materials, and different materials for the components can result in differences in power, energy density and cycling performance of batteries and therefore affect the use phase environmental burdens of BEVs [5], in our analysis we chose to study different cathode, anode and electrolyte chemistries that are commercially available for lithium ion batteries. Different pathways of cathode materials synthesis were also investigated in our study to better examine the use of organic solvents and process heat associated with different synthesis methods and their impact on the environmental footprints pertaining to the production phase. This study aims to provide insights from a life-cycle perspective into possible improvement of battery technology for BEVs in terms of cathode, anode and electrolyte materials manufacturing.

2.2 Methodology

2.2.1 Goal and scope of study

This study assesses the environmental footprints of different materials for components of Li-ion batteries that are in mass commercial production currently. Cathode materials of interest include $LiCoO_2$, $LiMn_2O_4$, $LiCoMnO_4$, $LiNiMnO_4$ and $LiFePO_4$. In order to analyze the difference between wet chemistry and dry chemistry, especially to investigate the environmental impacts resulted from organic solvents use and process heat in the synthesis process, the industry-wide applied calcination and sol-gel pathways are considered for cathode materials. Anode materials involve $LiTi_5O_{12}$, LiC_6 and graphite. Electrolytes investigated include $LiClO_4$, $LiBF_4$, $LiAsF_6$ and $LiPF_6$. Following the operation guide based on ISO standards [6], a streamlined life cycle approach is employed in this study, with the focus on the major life cycles stages constituting battery manufacturing, which begin with raw material extraction and end with production of battery components materials. The complete system flow diagram is depicted in the supplementary document (SD), Figure S1. The cut-off criteria is set to be 1%, so end-of-life of the materials involved in the manufacturing process is not considered due to their relatively small contribution to the total environmental impacts. For the same reason, the LCA of machineries and vehicles for transportation involved in the manufacturing process is not included in this work, while the machinery consumptions of electricity and natural gas, as well as the freighter consumptions of fuel are incorporated. As the focus of the study is the manufacturing process, and the overarching goal is to identify opportunities for greener manufacturing of the active materials for LIB components, the functional unit is chosen to be 1kg battery component material produced for a more directly perceivable comparison, without further consideration of the electrochemical characteristics of different materials. It is however, expected that the electrochemical properties of these active materials would become consequential if the use phase of battery is of concern. Therefore, in chapter 3 where the use phase of BEV is modeled, the functional unit is modified to account for the impact of the electrochemical properties.

2.2.2 Life cycle inventory (LCI) analysis

The production of each active cathode material using either calcination or sol-gel pathway is approximated by corresponding laboratory synthesis method reported in literature [7], [8], [9], [10], [11], [12], [13], [14], [15] and [16], assuming 95% yield. Synthesis conditions of each method are summarized in the SD, Table S1. Among anode materials, $LiTi_5O_{12}$ is assumed to be prepared via a calcination pathway [17]; LiC_6 is represented by a stoichiometric mixture of lithium and regular graphite, and the active material of graphite anode is assumed to be of battery grade. Electrolytes are approximated by the life-cycle inventory of $LiPF_6$ reported by Notter *et al* [4], with revisions of material and energy inputs according to industrial scale preparation methods reported in literature [18].

Production of all battery materials is assumed to take place in China. Material and energy inputs are obtained from Ecoinvent 2.2 database [19] due to better data availability. Energy consumptions of major production steps such as sintering and drying are estimated by the average of comparable industrial processes [20]. Materials inputs that are not found in Ecoinvent database are either substituted by similar chemicals, or synthesized according to industrially available method [21] using existing materials in the database. Organic chemical plants taken from Ecoinvent database are used to account for infrastructures involved in manufacturing, while transportation of materials are calculated based on Ecoinvent standard transport distance for chemicals and metals. The details on assumptions and LCI tables of all the materials studies can be found in the SD, (Tables S2-S29).

2.2.3 Life cycle impact assessment (LCIA)

Since more than a dozen of materials are compared all at once in this study, it would be desirable to get a straightforward yet comprehensive representation of the environmental impacts of these different battery component materials. The method of Ecoindicator 99 with the hierarchic perspective and average weighting (EI99 H/A) [22], which folds into human health damage, ecosystem quality impairment and resources depletion, and expresses the results in a composite single score, is therefore selected to evaluate the environmental impacts of each material. It should be pointed out that however, the convenience of the single score comes at the cost of the controversial use of weighting, in which weighting values are assigned to three damage categories of human health, ecosystem quality and resources based on educated yet subjective estimates of their relative importance with regard to the total environmental impacts. In this study, a sensitivity analysis to weighting values is conducted to examine the impact of valuesphere input and test the robustness of the results.

As two widely used midpoint indicators, Cumulative Energy Demand (CED) v 1.07and IPCC 2007 100-year Global Warming Potential (GWP) are also selected to assess the environmental burdens of each material. Since the life cycle assessment entails extensive calculations, SimaPro 7.2 [23] is employed to facilitate the study.

2.3 Results and Discussion

2.3.1 Significance in environmental impacts on the component level

Figure 2-1, 2-2 and 2-3 depict the environmental impacts as CED, GWP and single score evaluated by Ecoindicator 99 for all the materials investigated in this study respectively. Table S30 in the SD also lists the environmental impacts of all materials in single score, broken up by impact categories. Considering that in an automobile battery, the mass ratio of active cathode material to active anode material is around 1.5[24], it can be asserted that the active materials of cathode generally play a more important role in the environmental burden of LIBs than those of anode, as Notter *et al* [4] and Majeau-Bettez *et al* [3] both suggested. Electrolyte, especially those containing fluorine, are also major contributors to the total environmental impacts if evaluated on a same mass basis. However, electrolyte of LIBs typically consists of the lithium salts and organic solvents, and organic solvents outweigh lithium salts. In addition, the mass ratio of electrolyte to cathode material ranges between 45-87% in a LIB for automobile applications [24]. These two factors render active electrolyte materials minor contributors to the total environmental impacts resulted from LIB manufacturing.

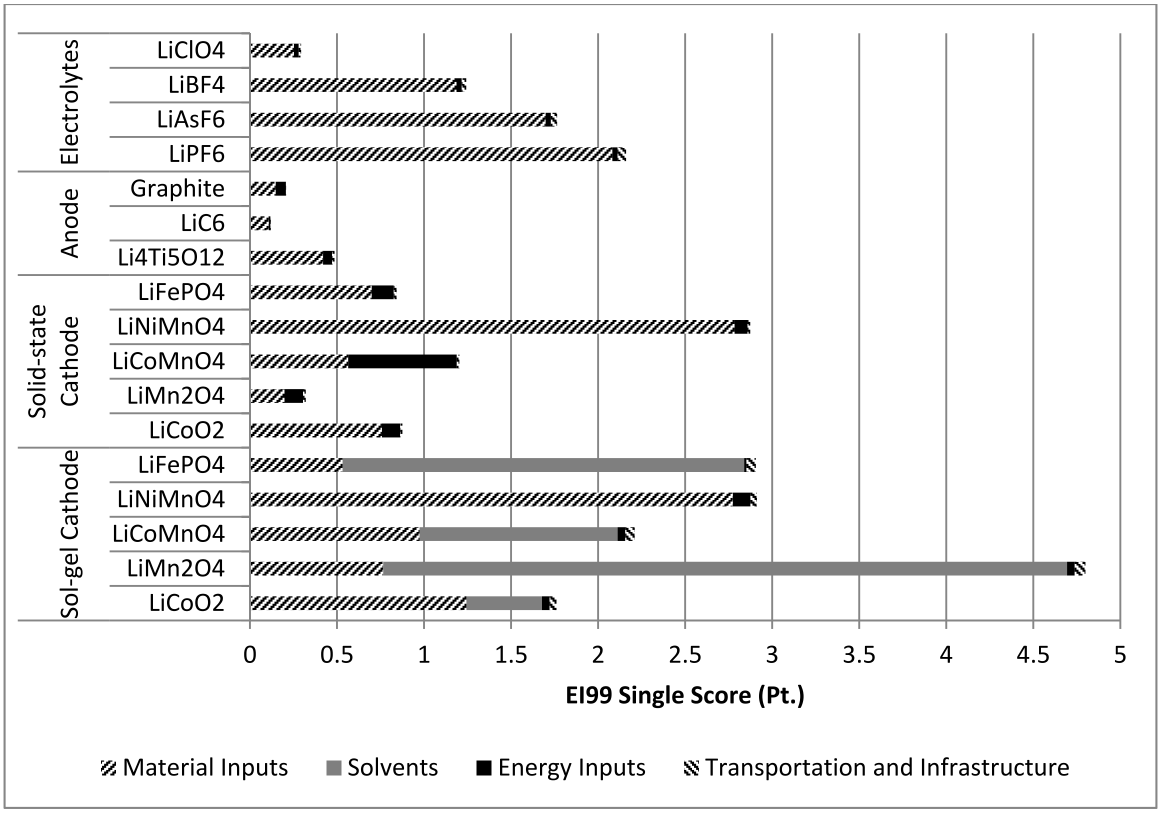

Figure 2-1. Environmental impacts from production of 1kg material in single point by EI99 H/A

2.3.2 Impact of cathode material chemistries and synthesis pathways

Looking at active materials of cathode alone, for calcination pathway, $LiMn_2O_4$ and $LiFePO_4$ both lead to smaller environmental impacts compared with other cathode chemistries. This is largely due to the chemical characteristics of the starting materials. Cadmium emissions associated with the mining of nickel and cobalt cause substantial damage to the environmental in forms of carcinogens and respiratory inorganics. The two categories respectively account for more than 30 percent of the EI99 single score of the least environmental-benign $LiNiMnO_4$. Therefore, cathode materials containing nickel and cobalt have higher impact scores overall. This is consistent with the finding of Majeau-Bettez *et al* [3]. It should be noted that, however, although $LiCoO_2$ also appears to be environment favorable, the environmental impacts of cobalt-containing compounds may have been underestimated, because of incompleteness of cobalt data, especially emission data, in the Ecoinvent database. Process heat has notable contribution to the environmental burdens of cathode materials also. As the material requiring the most energy in the manufacturing process, $LiCoMnO_4$ ranks first among all the cathode chemistries in CED and GWP, and second in terms of single score, with 60 percent of total environmental impact attributed to process heat input.

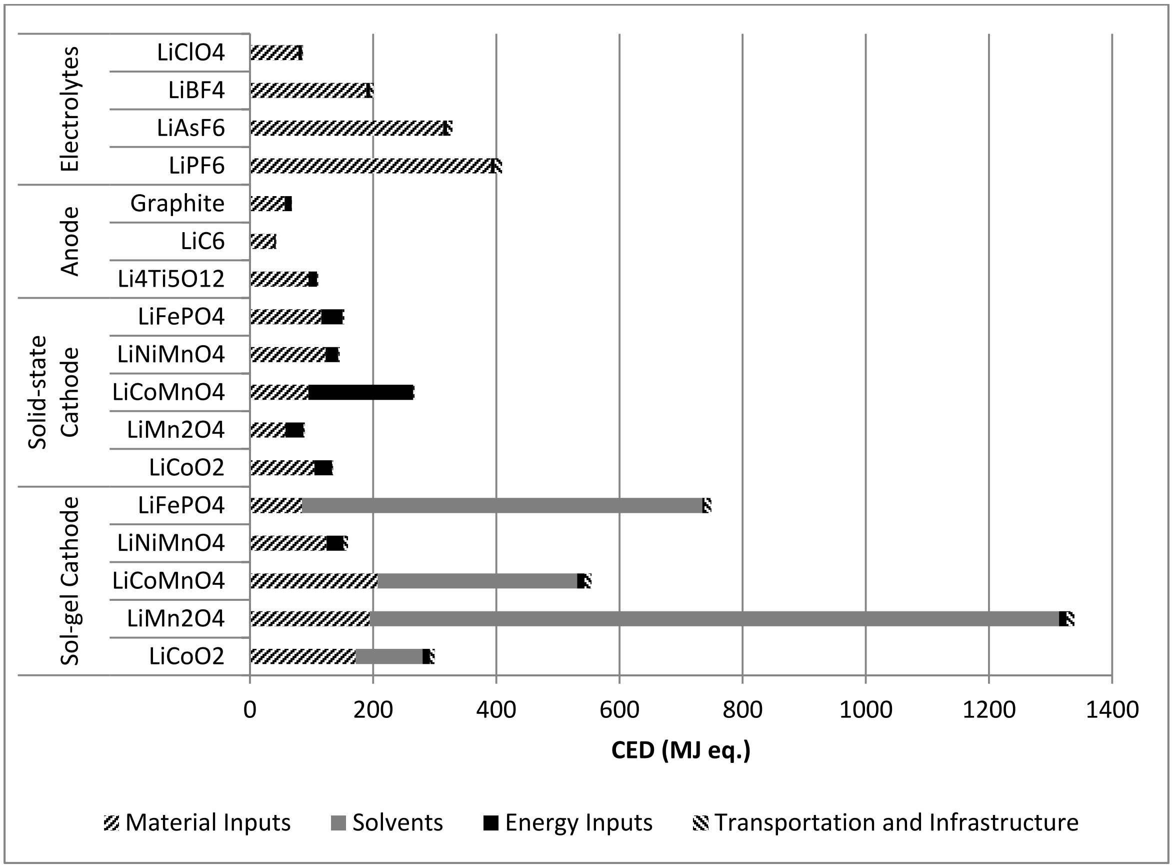

Figure 2-2.Environmental impacts from production of 1kg material in MJ equivalent by CED

As for the sol-gel pathway, the environmental impacts of $LiFePO_4$, $LiCoMnO_4$ and $LiMn_2O_4$ production are all dominated by organic solvent use. Since organic solvents result in significant impact with regard to respiratory organics, climate change and fossil fuels and therefore doubled the total impacts in most cases, all the cathode materials produced via sol-gel pathway have higher environmental burdens compared to their counterparts prepared by solid state pathway, with the exception of $LiNiMnO_4$, the preparation of which does not require organic solvents. Also, the previous dominance of starting materials characteristics in the environmental footprint now gives way to that of organic solvents. $LiNiMnO_4$, which has the highest score in the calcination based comparison, now becomes the most favorable cathode material due to zero organic solvents use.

2.3.3 Impact of anode and electrolyte chemistries

For anode, the production of LiC_6 seems to cause the minimum environmental damage, while the process heat input for $Li_4Ti_5O_{12}$ manufacturing greatly drives up the environmental impact. However, since a $Li_4Ti_5O_{12}$ anode makes the use of aluminum as anode current collector possible [25], $Li_4Ti_5O_{12}$ may be competitive as active anode material considering the substantial environmental impact imposed by copper current collector as reported by Notter *et al* [4]. Graphite anode material, assuming to be in the form of fine particles, requires considerable consumption of coke in the preparation process, and therefore ranks second in terms of environmental impact, especially in the damage category of respiratory inorganics.

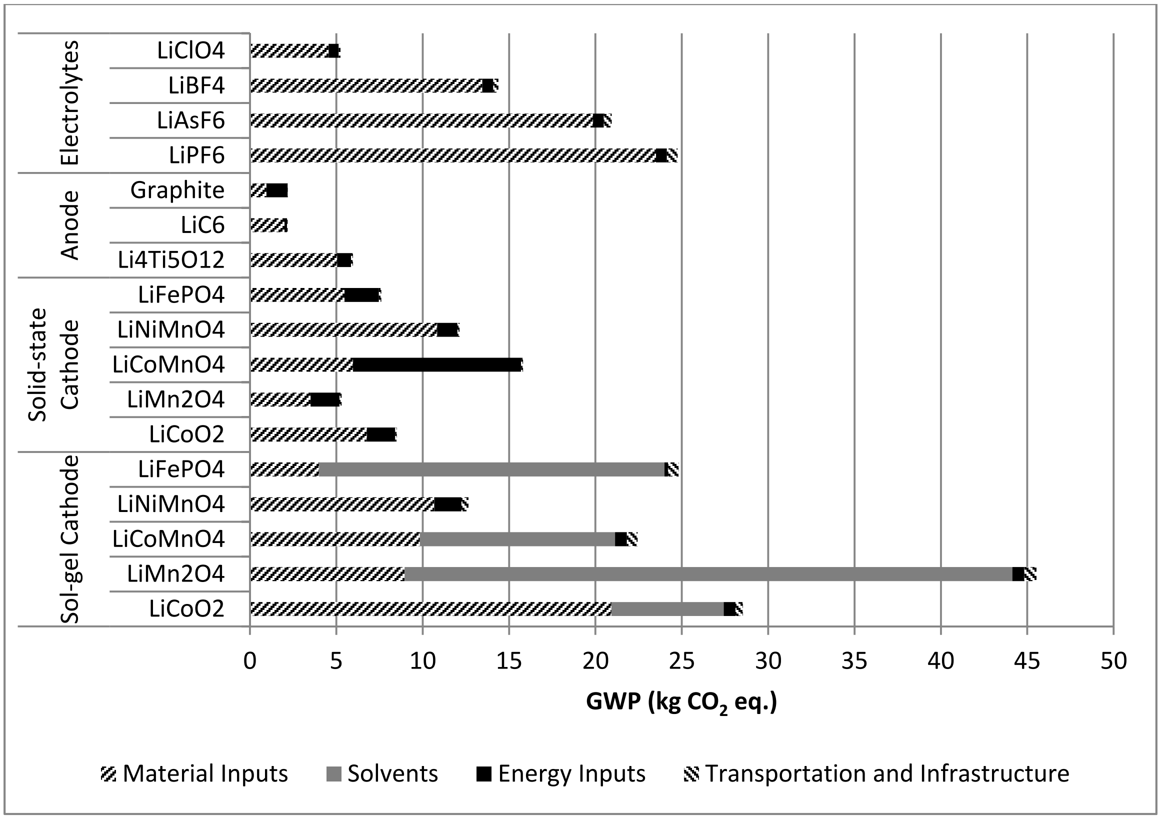

Figure 2-3. Environmental impacts from production of 1kg material in kg CO_2 equivalent by GWP

For electrolytes, $LiClO_4$ appears to be the most environment benign material, followed by $LiBF_4$, $LiAsF_6$ and $LiPF_6$. The environmental impacts of those materials are largely driven by the fluorine content coming from the fluoric acid use in the preparation processes, which results in sizable contribution to the overall eco-score in the damage categories of fossil fuels and respiratory inorganics. Although $LiAsF_6$ stands out in terms of ecotoxicity due to the arsenic content, it's outweighed by the impacts associated with excessive fluoric acid use in the manufacturing of $LiPF_6$.

2.3.4 Sensitivity to technosphere inputs

Because of its importance in the manufacturing of LIB, a sensitivity analysis has been carried out for organic solvents use in the sol-gel process. A scenario of 80% organic solvent recycling has been constructed. With this recycling rate representing U.S. industrial average reported by an EPA report [26], the environmental impacts expressed in single score have been reduced by 15%-65%. Specifically, with a recycling rate of 88.5% for $LiCoMnO_2$, and 89.5% for $LiFePO_4$, the cathode materials prepared by sol-gel method would result in the same environmental impact as their counterparts prepared via calcination pathways.

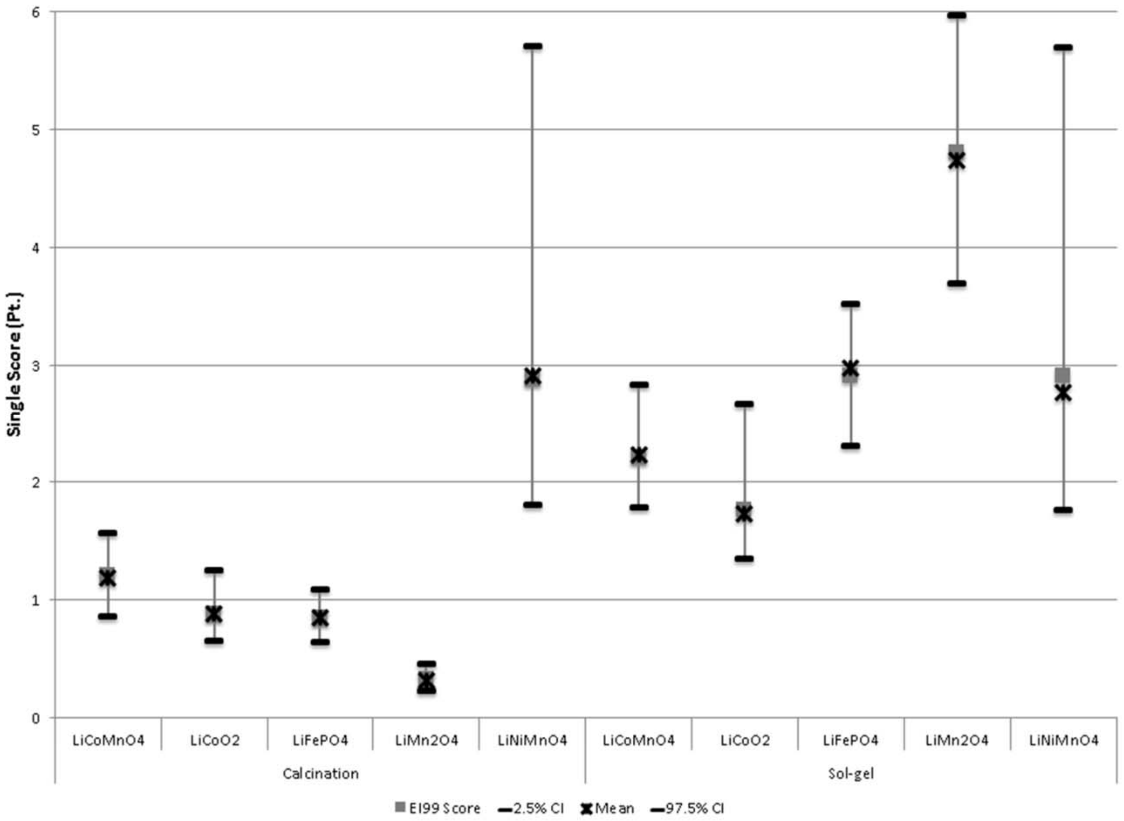

Figure 2-4.Results of Monte Carlo Simulation

As LCA analysis has its inherent uncertainties, stochastic modeling has also been conducted to deal with parameter uncertainty associated with the technosphere. Monte

Carlo simulation is applied to the material and energy inputs of cathode materials prepared via both pathways, with 100 random samplings as recommended by Kennedy *et al* [27] and Steen [28] from distributions and acceptable ranges of input values specified in Ecoinvent database. Results of the stochastic modeling are presented in Figure 2-4. The results confirm that $LiMn_2O_4$ is the most favorable cathode materials prepared by calcination method, and that calcination synthesis method offers an opportunity to reduce the environmental burden of LIB manufacturing. On the other hand, the results also suggest that there's great uncertainty associated with sol-gel synthesis pathways, largely due to organic solvent use. The uncertainty analysis again emphasizes the importance of reliable organic solvent use data in the LCA of LIB manufacturing.

2.3.5 Sensitivity to valuesphere inputs

In order to obtain single score results by EI 99 method, weighting values need to be assigned to human health, ecosystem quality and resources respectively. Since the use of weighting methods in the life cycle impact assessment is a controversial issue, a sensitivity analysis has been carried out to study the robustness of the results against variations in weighting value choices. The results of the sensitivity analysis are depicted in Figure 2-5. It can be observed from the four triangular plots that the conclusions of the most environment favorable electrolyte material and cathode material prepared by calcination pathway, as well as the least environment beneficial anode material and cathode materials synthesized via both pathways well stand the test. In addition, the ranking of $LiBF_4$, $LiCoMnO_4$ prepared by calcination and $LiFePO_4$ manufactured via the wet route show no sensitivity to the choices of weighting values. Nonetheless, the third place for anode material and sol-gel cathode material, second place for electrolyte material and fourth place for calcination cathode material are subjected to changes with weighting values.

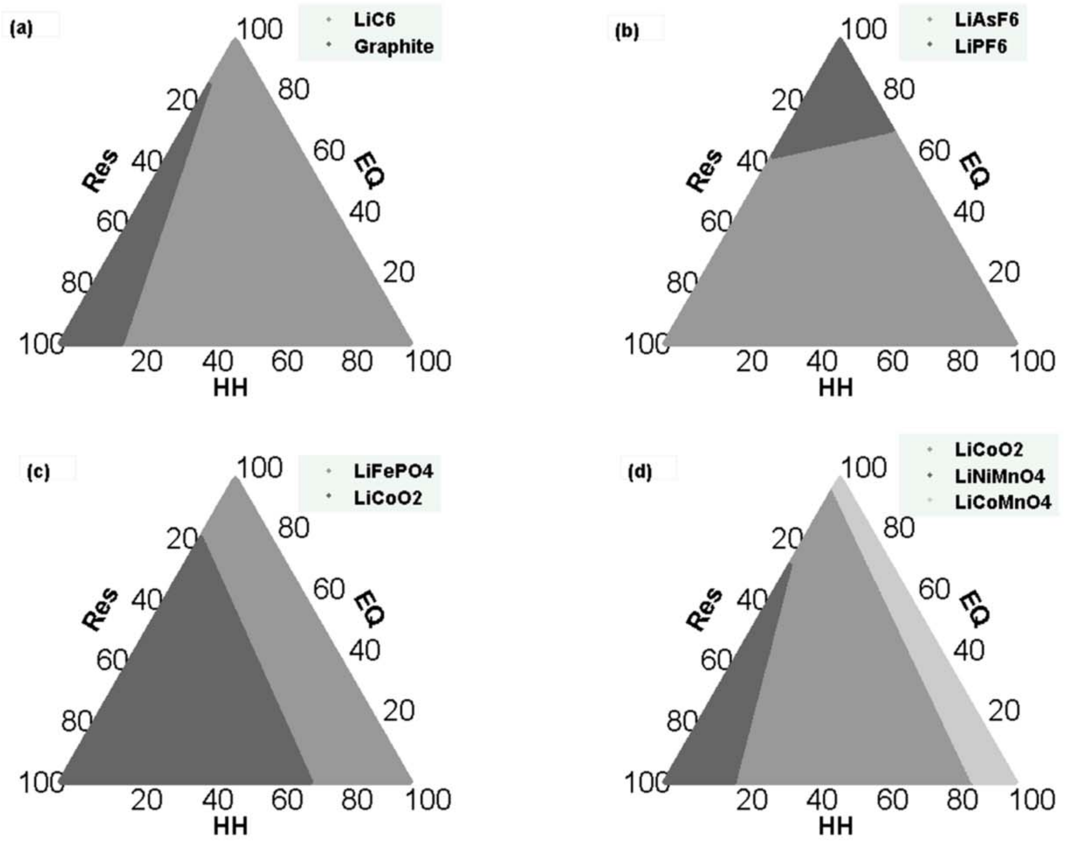

Figure 2-5. Impact of weighting value choices on LCIA results interpretations. (a). Most environment-benign anode material; (b). Least environment-benign electrolyte salt; (c). 2nd most environment-benign cathode material prepared by calcination method; (d). Most environment-benign cathode material prepared by sol-gel method change with weighting values, while other rankings remain the same regardless of changes in weighting values.
Note: HH: human health, EQ: ecosystem quality, Res: resource depletion

2.4 Conclusions

Despite the uncertainty associated with the LCA results, it can be concluded that the greatest potential for improving the eco-design and manufacturing of LIBs lies in reduction, if not elimination of organic solvent use in the preparation of cathode materials. Reduction in process heat input could contribute to the sustainable manufacturing of LIBs. Opportunities for improvement also exist in the switch to a cathode material that does not contain nickel and cobalt.

References

[1]. P. Van Den Bossche, F. Vergels, J. Van Mierlo, J. Matheys, W. Van Autenboer, J. Power Sources.162 (2006) 913–919.
[2]. M. Zackrisson, L. Avellan, J. Orlenius, J. Clean. Prod. 18 (2010) 1519-1529.
[3]. G. Majeau-Bettez, T.R. Hawkins, A.H. Stromman, Environ. Sci. Technol. 45 (2011) 4548-4554.
[4]. D.A. Notter, M. Gauch, R. Widmer, P. Wager, A. Stamp, R. Zah, H.J. Althaus, Environ. Sci. Technol. 44 (2010) 6550–6556.
[5]. K. Ozawa Eds, Lithium Ion Rechargeable Batteries: Materials, Technology, and New Applications, WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010.
[6]. J.B. Guinee, Handbook of Life Cycle Assessment: Operation Guide to ISO standards, Kluwer Academic Publishers: Dordrecht, Netherlands, 2002.
[7]. Y.K. Sun, J. Power Sources. 83 (1999) 223-226.
[8]. Y.J. Park, J.G. Kim, M.K. Kim, H.T. Chung, H.G. Kim, Solid State Ionics. 130 (2000) 203-214.
[9]. Q.M. Zhong, A. Bonakdarpour, M.J. Zhang, Y. Gao, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 205-213.
[10]. N. Amdouni, F. Gendron, A. Mauger, H. Zarrouk, C.M. Julien, Mater. Sci. Eng. 129 (2006) 64-75.
[11]. M.A.E. Sanchez, G.E.S. Brito, M.C.A. Fantini, G.F. Goya, J.R. Matos, Solid State Ionics. 177 (2006) 497-500.
[12]. V. Berbenni, C. Milanese, G. Bruni, A. Marini, Mater. Chem. Phys.100 (2006) 251-256.
[13]. T. Li, W.H. Qiu, R.H. Zhao, H. Xia, H.L. Zhao, J.J. Liu, J.J. J. Univ. Sci. Technol. B. 15 (2008) 74-78.
[14]. T. Ohzuku, K. Ariyoshi, S. Yamamoto, Y. Makimura, Chem. Lett. 30 (2001) 1270-1271.
[15]. H. Kawai, M. Nagata, H. Tukamoto, A.R. West, Electrochem. Solid St. 1 (1998) 212-214.
[16]. A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224-A229.
[17]. T. Ohzuku, A. Ueda, N. Yamamoto, J. Electrochem. Soc. 142 (1995) 1431-1435.
[18]. D.T. Merish, S.D. Merish, R. Davis, D. Contractor, V.N. Plakhotnik, E. Shembel, N. Globa, In 17th Annual Battery Conference on Applications and Advances, Proceedings; Long Beach, CA 2002, 151-163.
[19]. *Overview and Methodology*; ecoinvent report No. 1. Swiss Centre for Life Cycle Inventories: Dübendorf, Switzerland, 2007 (last accessed 07/18/2013) http://www.ecoinvent.org/fileadmin/documents/en/01_OverviewAndMethodology.pdf
[20]. H.L. Brown, B.B. Hamel, B.A. Hedman, Energy Analysis of 108 Industrial Processes, The Fairmont Press, Inc.: Upper Saddle River, NJ, 1996.
[21]. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005.
[22]. *The Eco-indicator 99 A Damage Oriented Method for Life Cycle Impace Assessment;* Methodology report. Pre Consultants B.V.: Amersfoort, Netherlands, 2001 (last accessed 07/18/2013)
http://www.pre.nl/download/misc/EI99_methodology_v3.pdf
[23]. *Introduction into LCA SimaPro 7;* Pre Consultants B.V.: Amersfoort, The Netherlands, 2008 (last accessed 07/18/2013)
www.pre.nl/download/manuals/SimaPro7IntroductionToLCA.pdf
[24]. L. Gaines, P. Nelson, Lithium-ion batteries: possible materials issues. 13th International Battery Materials Recycling Seminar & Exhibit, 2009 (last accessed 07/18/2013)
http://www.transportation.anl.gov/pdfs/B/583.PDF

[25]. D. Peramunage, K.M. Abraham, J. Electrochem. Soc. 145 (1998) 2609-2615.
[26]. Technical Resource Document: Treatment Technologies for Solvent Containing Waste; United States Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, U.S., 1986.
[27]. D.J. Kennedy, D.C. Montgomery, B.H. Quay, Int. J. Life Cycle Ass. 1 (1996) 199-207.
[28]. B. Steen, J. Clean. Prod. 5 (1997) 255-262.

2.5 Supporting Information

2.5.1 System boundary and description

The system boundary of the study is depicted in Figure S2-1. The cut-off criteria is set to be 1%, suggesting processes and material/energy inputs whose contributions to the total environmental is less than 1% will not be included in the analysis. Therefore, end-of-life of the materials involved in the manufacturing process is not considered due to their relatively small contribution to the total environmental impacts, especially when a conversion rate of 95% is assumed. For the same reason, the LCA of machineries and vehicles for transportation involved in the life cycle is not included in this work, while the machinery consumptions of electricity and natural gas, as well as the freighter consumptions of fuel are incorporated.

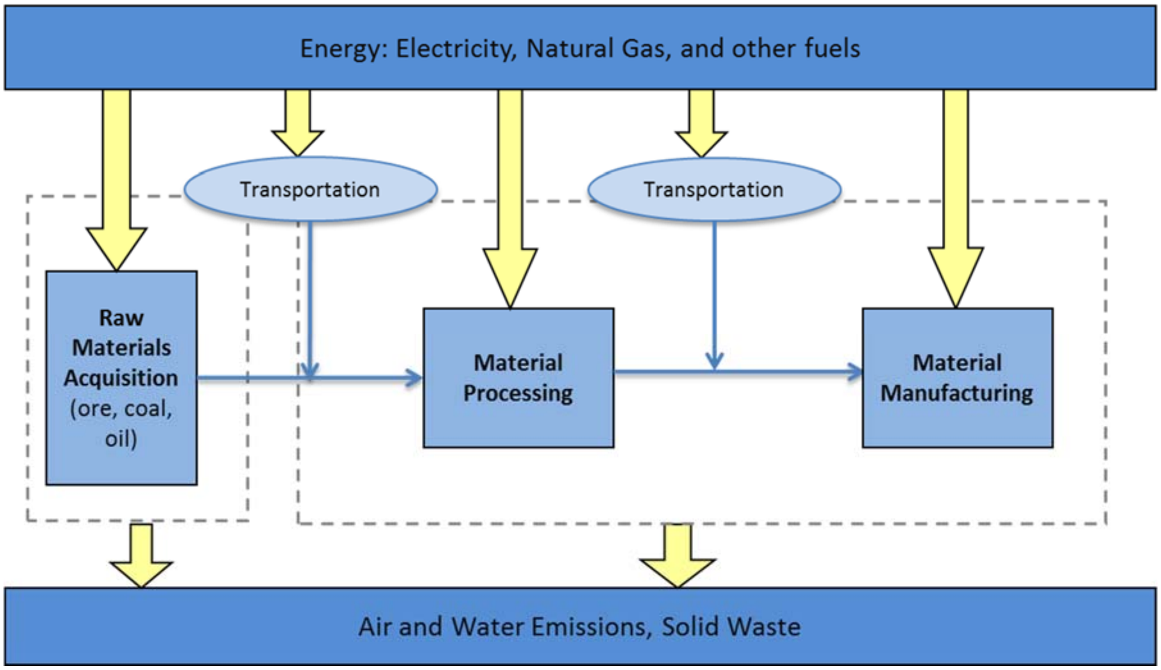

Figure S2-2. Process Flow Diagram

2.5.2 Inventory Tables

2.5.2.1 Inventory for active cathode materials

In order to analyze the difference between wet chemistry and dry chemistry, especially to investigate the environmental impacts resulted from organic solvents use and process heat in the synthesis process, the industry-wide applied solid-state and sol-gel pathways are considered for cathode materials. Each pathway is approximated by corresponding laboratory synthesis method reported in literature (Table S2-1).

Table S2-1. Synthesis Conditions of Cathode Materials as Reported in Literature

	Material	Starting Materials	Solvents	Additives	Synthesis Condition
Sol-gel	LiCoO2	Li, Co nitrates	Water	Poly acrylic acid, nitric acid	Evaporate at 80 deg C, fire at ~600 deg C for 10h
	LiMn2O4	Li, Mn acetates (0.3M)	1-butanol and acetic acid(3:1)	None	Magnetic stir 10h, filter, deposit at 80 deg C, dry at ~300 deg C
	LiNiMnO4	LiOH, $Ni(NO_3)2.6H_2O$, MnO_2	Water (0.1M, 150ml)	Carbon black	Stir 1h, fire at ~600 deg C for 24h
	LiCoMnO4	Li, Co, Mn acetate	Water, citric acid	None	Stir 6h, evaporate at ~80 deg C, fire at ~600 deg C
	LiFePO4	$LiOH.H_2O$, H_3PO_4, $Fe(CH_3COO)_2$	Ethanol/ water (50%)	1-butanol or propanol(wash)	Stir 1h, fire at ~600 deg C for 2.5h
Solid state	LiCoO2	Li_2CO_3, Co	None	None	Heated at ~600 deg C for 12h
	LiMn2O4	Li2CO3, Mn2O3	None	None	Calcine at ~600 deg C for 18h
	LiNiMnO4	LiOH, $Ni(NO_3)_2.6H_2O$, MnO_2	None	None	Heated at 1000 deg C for 12h and then 700 deg C for 24h
	LiCoMnO4	Li_2CO_3, CoO, $MnCO_3$	None	None	Fired at 650 deg C for 2h, 800 deg C for 3d, and 600 deg C for 3d
	LiFePO4	$Fe(CH_3COO)_2$, $NH_4H_2PO_4$, Li_2CO_3	Acetone	Nitrogen atmosphere	Decomposed at 320 deg C for 10h and sintered at ~600 deg C for 24h

The database used in this study is Ecoinvent 2.2. Materials input are based on stoichiometric calculations, assuming 95% yield. For materials are nonexistent in Ecoinvent, inventories tables were first constructed based on industrially available synthesis method using existing materials in the database. Considering that these intermediate materials are usually coproduct in the refining process or other chemical production process, infrastructure and emissions are not included in the inventory to avoid double counting. A process heat input of 2 MJ is assumed for each of the intermediate product, to account for energy requirement for the operation of machineries.

For processes dedicated to the production of active cathode materials, the energy requirement of major production steps such as sintering and drying are estimated by the average of comparable industrial processes. Besides, an electricity input of 0.005 KW is assumed for each of the process as mechanical drive.

Table S2-2. Inventory Table for the Production of Nickel Oxide

	Value	Unit
Product		
Nickel Oxide	1	kg
Materials/fuels		
Nickel, 99.5%, at plant/GLO U	0.827	kg
Oxygen, liquid, at plant/RNA	0.225	kg
Electricity/heat		
Transport, lorry >16t, fleet average/RER U	0.105	tkm
Transport, freight, rail/RER U	0.21	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ

Table S2-3. Inventory Table for the Production of Nickel Nitrate

	Value	Unit
Products		
Nickel Nitrate	1	kg
Materials/fuels		
Nickel Oxide	0.43	kg
Nitric acid, 50% in H2O, at plant/RER U	1.452	kg
Electricity/heat		
Transport, freight, rail/RER U	1.129	tkm
Transport, lorry >16t, fleet average/RER U	0.188	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ

Table S2-4. Inventory Table for the Production of Cobalt Oxide

	Value	Unit
Products		
Cobalt Oxide	1	kg
Materials/fuels		
Cobalt, at plant/GLO U	0.828	kg
Oxygen, liquid, at plant/RER U	0.224	kg
Electricity/heat		
Transport, lorry >16t, fleet average/RER U	0.105	tkm

Transport, freight, rail/RER U	0.21	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ

Table S2-5. Inventory Table for the Production of Cobalt Nitrate

	Value	Unit
Products		
Cobalt Nitrate	1	kg
Materials/fuels		
Cobalt Oxide	0.43	kg
Nitric acid, 50% in H2O, at plant/RER U	1.452	kg
Electricity/heat		
Transport, lorry >16t, fleet average/RER U	0.188	tkm
Transport, freight, rail/RER U	1.129	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ

Table S2-6. Inventory Table for the Production of Cobalt Acetate

	Value	Unit
Products		
Cobalt Acetate	1	kg
Materials/fuels		
Cobalt, at plant/GLO U	0.351	kg
Acetic acid, 98% in H2O, at plant/RER U	0.729	kg
Oxygen, liquid, at plant/RER U	0.723	kg
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ
Transport, freight, rail/RER U	0.652	tkm
Transport, lorry >16t, fleet average/RER U	0.18	tkm

Table S2-7. Inventory Table for the Production of Manganese Sulfate

	Value	Unit
Products		
Manganese Sulfate	1	kg
Materials/fuels		
Sulphuric acid, liquid, at plant/RER U	0.683	kg
Manganese oxide (Mn2O3), at plant/CN U	0.551	kg
Electricity/heat		
Transport, lorry >16t, fleet average/RER U	0.1234	tkm
Transport, freight, rail/RER U	0.7404	tkm

Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ

Table S2-8. Inventory Table for the Production of Manganese Carbonate

	Value	Unit
Products		
Manganese Carbonate	1	kg
Materials/fuels		
Manganese Sulfate	1.382	kg
Soda, powder, at plant/RER U	0.769	kg
Water, deionised, at plant/CH U	5	kg
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ
Transport, freight, rail/RER U	4.291	tkm
Transport, lorry >16t, fleet average/RER U	0.715	tkm

Table S2-9. Inventory Table for the Production of Manganese Acetate

	Value	Unit
Products		
Manganese Acetate	1	kg
Materials/fuels		
Acetic acid, 98% in H2O, at plant/RER U	0.746	kg
Manganese Carbonate	0.7	kg
Electricity/heat		
Transport, freight, rail/RER U	0.868	tkm
Transport, lorry >16t, fleet average/RER U	0.145	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ

Table S2-10. Inventory Table for the Production of Lithium Nitrate

	Value	Unit
Products		
Lithium Nitrate	1	kg
Materials/fuels		
Lithium hydroxide, at plant/GLO U	0.397	kg
Nitric acid, 50% in H2O, at plant/RER U	1.922	kg
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ
Transport, freight, rail/RER U	1.391	tkm
Transport, lorry >16t, fleet average/RER U	0.232	tkm

Table S2-11. Inventory Table for the Production of Lithium Acetate

	Value	Unit
Products		
Lithium Acetate	1	kg
Materials/fuels		
Acetic acid, 98% in H2O, at plant/RER U	0.976	kg
Lithium carbonate, at plant/GLO U	1.18	kg
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ
Transport, freight, rail/RER U	1.2936	tkm
Transport, lorry >16t, fleet average/RER U	0.2156	tkm

Table S2-12. Inventory Table for the Production of Iron(II) Acetate

	Value	Unit
Products		
Iron(II) Acetate	1	kg
Materials/fuels		
Acetic acid, 98% in H2O, at plant/RER U	0.741	kg
Iron, sand casted/US	0.339	kg
Water, deionised, at plant/CH U	3.6	kg
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ
Transport, freight, rail/RER U	2.672	tkm
Transport, lorry >16t, fleet average/RER U	0.468	tkm

Table S2-13. Inventory Table for the Calnication of Lithium Cobalt Oxide

	Value	Unit
Products		
LiCoO2_calcination	1	kg
Materials/fuels		
Oxygen, liquid, at plant/RER U	0.7145	kg
Chemical plant, organics/RER/I U	4E-10	p
Cobalt, at plant/GLO U	0.634	kg
Lithium carbonate, at plant/GLO U	0.398	kg
Electricity/heat		
Transport, freight, rail/RER U	0.509	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	22.79	MJ
Transport, lorry >16t, fleet average/RER U	0.175	tkm
Electricity, medium voltage, at grid/CN U	0.005	kWh

Emissions to air		
Carbon dioxide, fossil	0.2366	kg
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.0516	kg

Table S2-14. Inventory Table for the Sol-gel Synthesis of Lithium Cobalt Oxide

	Value	Unit
Products		
LiCoO2_Sol-gel	1	kg
Materials/fuels		
Lithium nitrate	0.74	kg
Cobalt nitrate	1.97	kg
Chemical plant, organics/RER/I U	4.00E-10	p
Acrylic acid, at plant/RER U	1.47	kg
Nitric acid, 50% in H2O, at plant/RER U	1	kg
Water, deionised, at plant/CH U	5	kg
Electricity/heat		
Natural gas, burned in industrial furnace >100kW/RER U	10.002	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	6.108	tkm
Transport, lorry >16t, fleet average/RER U	1.018	tkm
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.1355	kg

Table S2-15. Inventory Table for the Calcination of Lithium Manganese Oxide

	Value	Unit
Products		
LiMn2O4_calcination	1	kg
Materials/fuels		
Oxygen, liquid, at plant/RER U	0.7145	kg
Nitrogen, liquid, at plant/RER U	0.786	kg
Chemical plant, organics/RER/I U	4E-10	p
Manganese oxide (Mn2O3), at plant/CN U	0.91817	kg
Lithium carbonate, at plant/GLO U	0.21486	kg
Electricity/heat		
Transport, freight, rail/RER U	0.9799	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	23.26	MJ

Transport, lorry >16t, fleet average/RER U	0.2634	tkm
Electricity, medium voltage, at grid/CN U	0.005	kWh
Emissions to air		
Carbon dioxide, fossil	0.12794	kg
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.056652	kg

Table S2-16. Inventory Table for the Sol-gel Synthesis of Lithium Manganese Oxide

	Value	Unit
Products		
LiMn2O4_Sol-gel	1	kg
Materials/fuels		
Lithium acetate	0.384	kg
Manganese acetate	2.012	kg
1-butanol, propylene hydroformylation, at plant/RER U	10.635	kg
Acetic acid, 98% in H2O, at plant/RER U	4.829	kg
Chemical plant, organics/RER/I U	4.00E-10	p
Electricity/heat		
Natural gas, burned in industrial furnace >100kW/RER U	10.002	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	10.7166	tkm
Transport, lorry >16t, fleet average/RER U	1.7861	tkm
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.1198	kg

Table S2-17. Inventory Table for the Calcination of Lithium Cobalt Manganese Oxide

	Value	Unit
Products		
LiCoMnO4_calcination	1	kg
Materials/fuels		
Cobalt oxide	0.4263	kg
Nitrogen, liquid, at plant/RER U	0.786	kg
Manganese carbonate	0.6543	kg
Lithium carbonate, at plant/GLO U	0.2105	kg
Chemical plant, organics/RER/I U	4E-10	p
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	135.809	MJ

Transport, lorry >16t, fleet average/RER U	0.208	tkm
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	0.932	tkm
Emissions to air		
Carbon dioxide, fossil	0.3755	kg
Heat, waste	0.18	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.064555	kg

Table S2-18. Inventory Table for the Sol-gel Synthesis of Lithium Cobalt Manganese Oxide

	Value	Unit
Products		
LiCoMnO4_Sol-gel	1	kg
Materials/fuels		
Lithium acetate	0.372	kg
Manganese acetate	0.974	kg
Acrylic acid, at plant/RER U	5	kg
Water, deionised, at plant/CH U	8	kg
Chemical plant, organics/RER/I U	4.00E-10	p
Cobalt acetate	0.996	kg
Electricity/heat		
Natural gas, burned in industrial furnace >100kW/RER U	10.002	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	9.205	tkm
Transport, lorry >16t, fleet average/RER U	1.5342	tkm
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.1171	kg

Table S2-19. Inventory Table for the Calcination of Lithium Nickel Manganese Oxide

	Value	Unit
Products		
LiNiMnO4_calcination	1	kg
Materials/fuels		
Oxygen, liquid, at plant/RER U	0.7145	kg
Ni(NO3)2	1.0413	kg
Chemical plant, organics/RER/I U	4E-10	p
Manganese oxide (Mn2O3), at plant/CN U	0.4502	kg
Lithium hydroxide, at plant/GLO U	0.1368	kg
Electricity/heat		

Transport, freight, rail/RER U	1.12	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	16.264	MJ
Transport, lorry >16t, fleet average/RER U	0.2634	tkm
Electricity, medium voltage, at grid/CN U	0.005	kWh
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.081415	kg

Table 2-20. Inventory Table for the Sol-gel Synthesis of Lithium Nickel Manganese Oxide

	Value	Unit
Products		
LiNiMnO4_Sol-gel	1	kg
Materials/fuels		
Lithium hydroxide, at plant/GLO U	0.135	kg
Nickel nitrate	1.03	kg
Manganese oxide (Mn2O3), at plant/CN U	0.444	kg
Water, deionised, at plant/CH U	8.021	kg
Chemical plant, organics/RER/I U	4.00E-10	p
Carbon black, at plant/GLO U	0.1	kg
Electricity/heat		
Natural gas, burned in industrial furnace >100kW/RER U	23.0274	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	5.8388	tkm
Transport, lorry >16t, fleet average/RER U	0.9731	tkm
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.08045	kg

Table S2-21. Inventory Table for the Calcination of Lithium Iron Phosphate

	Value	Unit
Products		
LiFePO4_calcination	1	kg
Materials/fuels		
Iron(II) acetate	1.1589	kg
Acetone, liquid, at plant/RER U	0.1	kg
Chemical plant, organics/RER/I U	4E-10	p
Monoammonium Phosphate	0.916	kg
Lithium carbonate, at plant/GLO U	0.2463	kg

Electricity/heat		
Transport, freight, rail/RER U	1.453	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	27.674	MJ
Transport, lorry >16t, fleet average/RER U	0.242	tkm
Electricity, medium voltage, at grid/CN U	0.005	kWh
Emissions to air		
Carbon dioxide, fossil	0.14645	kg
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.11606	kg

Table S2-22. Inventory Table for the Sol-gel Synthesis of Lithium Iron Phosphate

	Value	Unit
Products		
LiFePO4_Sol-gel	1	kg
Materials/fuels		
Lithium hydroxide, at plant/GLO U	0.16	kg
Iron Acetate	1.159	kg
Phosphoric acid, industrial grade, 85% in H2O, at plant/RER U	0.768	kg
Chemical plant, organics/RER/I U	4.00E-10	p
1-butanol, propylene hydroformylation, at plant/RER U	6.16	kg
Ethanol from ethylene, at plant/RER U	3.156	kg
Water, deionised, at plant/CH U	4	kg
Electricity/heat		
Natural gas, burned in industrial furnace >100kW/RER U	3.0238	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	9.1728	tkm
Transport, lorry >16t, fleet average/RER U	1.5288	tkm
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.06595	kg

2.5.2.2 Inventory for active anode materials

Table S2-23. Inventory Table for the Calcination of Lithium Titanium Oxide

	Value	Unit
Products		
Lithium Titanium Oxide	1	kg
Materials/fuels		
Lithium hydroxide, at plant/GLO U	0.22	kg
Titanium dioxide, production mix, at plant/RER U	0.916	kg
Nitrogen, liquid, at plant/RER U	0.786	kg
Chemical plant, organics/RER/I U	4.00E-10	p
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	11.16	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh
Transport, freight, rail/RER U	0.8388	tkm
Transport, lorry >16t, fleet average/RER U	0.1922	tkm
Emissions to air		
Heat, waste	0.018	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.0568	kg

Table S2-24. Inventory Table for the Production of Lithiated Graphite

	Value	Unit
Products		
LiC6	1	kg
Materials/fuels		
Lithium, at plant/GLO U	0.0933	kg
Graphite, at plant/RER U	0.9594	kg
Electricity/heat		
Transport, lorry >16t, fleet average/RER U	0.1053	tkm
Transport, freight, rail/RER U	0.6318	tkm

The lithiated graphite is represented by a stoichiometric mixture of lithium and graphite. As this mixing process doesn’t involve any peculiar industrial process, no energy input and infrastructure is assumed in the production process. Also, the mixing process doesn’t seem to give off any consequential emissions, which are therefore included in the inventory.

2.5.2.3 Inventory for active electrolyte materials

Table S2-25. Inventory Table for the Production of Arsenic Pentafluoride

	Value	Unit
Products		
Arsenic pentafluoride	1	kg
Materials/fuels		
Fluorine, liquid, at plant/RER U	0.7059	kg
Arsine, at plant/GLO U	0.483	kg
Electricity/heat		
Heat, natural gas, at industrial furnace >100kW/RER U	2	MJ
Transport, lorry >16t, fleet average/RER U	0.119	tkm
Transport, freight, rail/RER U	0.238	tkm

Table S2-26. Inventory Table for the Production of Perchlorate Acid

	Value	Unit
Products		
Perchlorate acid	1	kg
Materials/fuels		
Chlorine, liquid, production mix, at plant/RER U	0.3718	kg
Water, deionised, at plant/CH U	0.7541	kg
Electricity/heat		
Electricity, medium voltage, at grid/GB U	5	kWh
Transport, lorry >16t, fleet average/RER U	0.113	tkm
Transport, freight, rail/RER U	0.527	tkm

As perchlorate acid is assumed to be produced using an electrochemical process, electricity input alone represents the energy requirement for this process.

Table S2-27. Inventory Table for the Production of Lithium Hexafluoroarsenate

	Value	Unit
Products		
Lithium hexafluoroarsenate, at plant/CN U	1	kg
Materials/fuels		
Hydrogen fluoride, at plant/GLO U	0.6122	kg
Nitrogen, liquid, at plant/RER U	0.0012506	kg
Lime, hydrated, packed, at plant/CH U	7.4373	kg
Chemical plant, organics/RER/I U	4E-10	p
Lithium fluoride, at plant/CN U	0.153	kg
Arsenic pentafluoride	1	kg
Electricity/heat		
Transport, freight, rail/RER U	5.5218	tkm
Transport, lorry >16t, fleet average/RER U	0.9203	tkm
Electricity, medium voltage, at grid/CN U	0.54074	kWh
Emissions to air		
Heat, waste	1.9466	MJ
Waste to treatment		
Disposal, limestone residue, 5% water, to inert material landfill/CH U	7.809165	kg
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.05765	kg

Table S2-28. Inventory Table for the Production of Lithium Perchlorate

	Value	Unit
Products		
Lithium perchlorate, at plant/CN U	1	kg
Materials/fuels		
Chemical plant, organics/RER/I U	4E-10	p
Lithium carbonate, at plant/GLO U	0.3657	kg
Perchlorate acid	0.9933	kg
Electricity/heat		
Transport, freight, rail/RER U	0.815	tkm
Transport, lorry >16t, fleet average/RER U	0.136	tkm
Electricity, medium voltage, at grid/CN U	0.5	kWh

Emissions to air		
Carbon dioxide, fossil	0.21744	kg
Heat, waste	1.79994	MJ
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.06795	kg

Table S-29. Inventory Table for the Production of Lithium Tetrafluoroborate

	Value	Unit
Products		
Lithium tetrafluoroborate, at plant/CN U	1	kg
Materials/fuels		
Hydrogen fluoride, at plant/GLO U	1.2766	kg
Nitrogen, liquid, at plant/RER U	0.0012506	kg
Lime, hydrated, packed, at plant/CH U	5.9204	kg
Chemical plant, organics/RER/I U	4E-10	p
Lithium fluoride, at plant/CN U	0.319	kg
Boron trifluoride, at plant/GLO U	0.8344	kg
Electricity/heat		
Transport, freight, rail/RER U	1.458	tkm
Transport, lorry >16t, fleet average/RER U	0.9867	tkm
Electricity, medium voltage, at grid/CN U	0.54074	kWh
Emissions to air		
Heat, waste	1.9466	MJ
Waste to treatment		
Disposal, limestone residue, 5% water, to inert material landfill/CH U	6.21642	kg
Disposal, inert waste, 5% water, to inert material landfill/CH U	0.05767	kg

2.5.3 Results

2.5.3.1 General Results

Table S2-30. LCIA of Battery Component Materials in Single Score by Impact Categories

		Carcinogens	Resp. organics	Resp. inorganics	Climate change	Radiation	Ozone layer	Ecotoxi-city	Acidifica-tion/ Eutrophi-cation	Land use	Minerals	Fossil fuels	Total
Electrolytes	LiPF6	2.76E-01	2.98E-04	9.92E-01	1.36E-01	5.72E-03	1.81E-04	7.80E-02	6.50E-02	3.61E-02	4.08E-02	5.39E-01	2.17E+00
	LiAsF6	3.36E-01	2.49E-04	5.21E-01	1.14E-01	4.74E-03	6.07E-05	3.07E-01	3.88E-02	1.72E-02	1.96E-02	4.14E-01	1.77E+00
	LiBF4	1.53E-01	1.90E-04	5.76E-01	7.85E-02	2.28E-03	2.90E-05	4.09E-02	3.91E-02	1.62E-02	2.28E-02	3.22E-01	1.25E+00
	LiClO4	5.02E-02	4.21E-05	8.11E-02	2.84E-02	1.01E-03	3.37E-05	9.17E-03	7.96E-03	4.31E-03	3.76E-03	1.08E-01	2.94E-01
Anodes	Graphite	2.63E-02	5.28E-04	1.30E-01	1.16E-02	7.30E-05	5.73E-06	4.11E-03	4.45E-03	3.94E-03	2.47E-04	2.63E-02	2.08E-01
	$Li_4Ti_5O_{12}$	3.97E-02	9.16E-05	1.34E-01	3.31E-02	8.03E-04	2.65E-05	1.05E-02	9.82E-03	4.49E-03	4.65E-03	2.60E-01	4.97E-01
	LiC_6	2.12E-02	1.54E-05	2.80E-02	1.02E-02	6.72E-04	6.00E-06	4.23E-03	2.42E-03	1.19E-03	1.05E-03	3.31E-02	1.02E-01
Cathodes (solid-State)	$LiCoMnO_4$	6.68E-02	3.06E-04	2.50E-01	8.30E-02	1.06E-03	4.33E-05	1.53E-02	2.56E-02	2.55E-02	1.23E-02	6.73E-01	1.15E+00
	$LiCoO_2$	9.25E-02	3.53E-04	3.74E-01	4.73E-02	1.25E-03	2.05E-05	1.89E-02	3.71E-02	3.78E-02	1.14E-02	2.68E-01	8.88E-01
	$LiFePO_4$	4.59E-02	1.57E-04	1.14E-01	3.29E-02	5.13E-04	1.86E-05	1.42E-02	8.09E-03	5.04E-03	5.56E-03	3.33E-01	5.60E-01
	$LiMn_2O_4$	4.18E-02	5.79E-05	5.75E-02	2.95E-02	9.46E-04	1.20E-05	9.31E-03	5.74E-03	5.68E-03	1.12E-02	1.69E-01	3.30E-01
	$LiNiMnO_4$	9.32E-01	2.02E-04	1.04E+00	6.95E-02	1.12E-03	2.04E-05	1.94E-01	6.77E-02	1.23E-02	2.76E-01	2.92E-01	2.89E+00
Cathodes (sol-gel)	LiCoMnO4	1.40E-01	7.38E-04	3.92E-01	1.21E-01	2.38E-03	3.49E-05	3.44E-02	3.76E-02	3.16E-02	2.30E-02	1.43E+00	2.21E+00
	LiCoO2	1.24E-01	5.37E-04	5.57E-01	1.63E-01	1.61E-03	3.37E-05	3.88E-02	7.13E-02	4.54E-02	2.07E-02	7.38E-01	1.76E+00
	LiFePO4	2.32E-01	1.50E-03	2.83E-01	1.34E-01	1.22E-03	5.33E-05	3.50E-02	2.41E-02	3.14E-02	1.52E-02	2.15E+00	2.91E+00
	$LiMn_2O_4$	2.23E-01	2.30E-03	4.77E-01	2.45E-01	4.13E-03	1.29E-04	7.25E-02	4.41E-02	3.39E-02	3.99E-02	3.66E+00	4.80E+00
	$LiNiMnO_4$	9.19E-01	2.12E-04	1.04E+00	7.11E-02	9.83E-04	2.54E-05	1.91E-01	6.75E-02	1.26E-02	2.73E-01	3.41E-01	2.91E+00

2.5.3.2 Monte Carlo Simulation

To deal with uncertainties associated with assumptions of input values, Monte Carlo simulation with 100 random samplings is applied to each of the active cathode materials. To implement Monte Carlo in SimaPro, for each data entry, a lognormal distribution is assumed; six uncertainty factors are assigned based on data quality evaluated by six characteristics specified in the Pedigree matrix by Weidema and Wesnaes; one basic uncertainty factor is assigned automatically by SimaPro according to the type of data; then the square of the geometric standard deviation is calculated from the seven uncertainty factors. The Monte Carlo simulation subsequently samples randomly from a range of possible values as described by the distribution and geometric standard deviation, and in the end returns uncertainties as statistics of the 100 simulations. The Result of the Monte Carlo simulation is summarized in Figure S2.

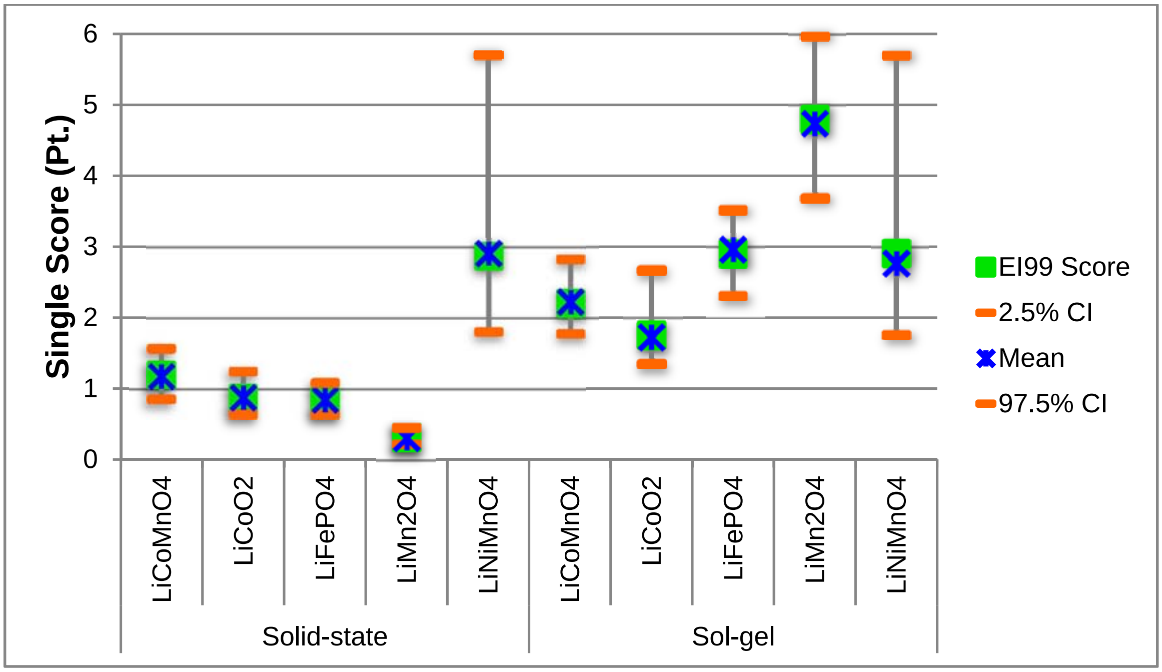

Figure S-3. Results of Monte Carlo Simulation

References

Amdouni, N.; Gendron, F.; Mauger, A.; Zarrouk, H.; Julien, C.M. $LiMn_{2-y}Co_yO_4(0 \leq y \leq 1)$ intercalation compounds synthesized from wet-chemical route. *Mater. Sci. Eng*. 2006, 129, 64-75.

Berbenni, V.; Milanese, C.; Bruni, G.; Marini, A. Solid state synthesis of stoichiometric $LiCoO_2$ from mechanically activated Co-Li_2CO_3 mixtures. *Mater. Chem. Phys.* 2006, 100, 251-256.

Brown, H.L.; Hamel, B.B.; Hedman, B.A. *Energy Analysis of 108 Industrial Processes*. The Fairmont Press, Inc.: Upper Saddle River, NJ, 1996.

Gaines, L.; Cuenca, R. *Cost of Lithium-Ion Batteries for Vehicles*; Center for Transportation Research, Energy System Division, Argonne National Laboratory, Illinois, U.S., 2000.

Kawai, H.; Nagata, M.; Tukamoto, H.; West, A.R. A new lithium cathode $LiCoMnO_4$: toward practical 5V lithium batteries. *Electrochem. Solid St*. 1998, 1, 212-214.

Kapusta, J. P.T. Cobalt production and markets: a brief overview. *JOM_J Min. Met. Mat. S.* 2006, 58, 33-36.

Life Cycle Assessment of Nickel Products; Final report. Ecobalance, Inc., Maryland, U.S., 2000.

Li, T.; Qiu, W.H.; Zhao, R.H.; Xia H.; Zhao, H.L.; Liu, J.J. Effects of sintering time on the electrochemical properties of spinel $LiMn_2O_4$ synthesized by solid-state reaction. *J. Univ. Sci. Technol. B.* 2008, 15, 74-78.

Merish, D.T.; Merish, S.D.; Davis, R.; Contractor, D.; Plakhotnik, V.N.; Shembel, E.; Globa, N. Commercal scale preparation, properties and the performance of $LiAsF_6$, $LiPF_6$, $LiBF_4$ electrolytes in secondary lithium ion and lithium cells. In *17th Annual Battery Conference on Applications and Advances, Proceedings*; Long Beach, CA 2002; pp 151-163.

Nelson, P.; Amine, K.; Yomoto, K. Advanced Lithium-ion Batteries for Plug-in Hybrid-Electric Vehicles. 23rd International Electric Vehicle Symposium (EVS23), Anaheim, CA, Dec 2-5, 2007.

Ohzuku, T.; Ariyoshi, K.; Yamamoto, S.; Makimura, Y. A 3-Volt lithium-ion cell with $Li[Ni_{1/2}Mn_{3/2}]O_4$ and $Li[Li_{1/3}Ti_{5/3}]O_4$: a method to prepare stable positive-electrode material of highly crystallized $Li[Ni_{1/2}Mn_{3/2}]O_4$. *Chem. Lett*. 2001, 30, 1270-1271.

Ohzuku, T.; Ueda, A.; Yamamoto, N. Zero-strain insertion material of $Li[Li_{1/3}Ti_{5/3}]O_4$ for rechargeable lithium cells. *J. Electrochem. Soc*. 1995, 142, 1431-1435.

Park, Y.J.; Kim, J.G.; Kim, M.K.; Chung, H.T.; Kim, H.G. Preparation of $LiMn_2O_4$ by a sol-gel method. *Solid State Ionics*. 2000, 130, 203-214.

Sanchez, M.A.E.; Brito, G.E.S.; Fantini, M.C.A.; Goya, G.F.; Matos, J.R. Synthesis and characterization of $LiFePO_4$ prepared by sol-gel technique. *Solid State Ionics*. 2006, 177, 497-500.

Shedd, K.B. The Materials Flow of Cobalt in the United States. United States Department of the Interior, Bureau of Mines, U.S., 1993.

Sun, Y.K. Cycling behavior of $LiCoO_2$ cathode materials prepared by PAA-assisted sol-gel method for rechargeable lithium batteries. *J. Power Sources*. 1999, 83, 223-226.

Synthesis of Iron (II) acetate hydrate (ferrous acetate).
http://www.ims.demokritos.gr/people/tbou/iron_acetate.html

Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005.

Weidema, B.P.; Wesnaes, M.S. Data quality management for life cycle inventories - an example of using data quality indicators. *J. Clean. Prod.* 1996, 4,167-174.

Yamada, A.; Chung, S.C.; Hinokuma, K. Optimized $LiFePO_4$ for lithium battery cathodes. *J. Electrochem. Soc*. 2001, 148, A224-A229.

Zhong, Q.M.; Bonakdarpour, A.; Zhang, M.J.; Gao, Y.; Dahn, J.R. Synthesis and electrochemistry of $LiNi_xMn_{2-x}O_4$. *J. Electrochem. Soc*. 1997, 144, 205-213.

Chapter 3

Sustainability of Battery Electric Vehicles Propelled by Lithium-ion Batteries: Use-phase

3.1 Introduction

As an effective transportation means to reduce greenhouse gas emissions and energy consumption, alternative fuel vehicles (AFVs) has received wide attention from both academia and industry. In order to evaluate the environmental friendliness of AFVs and aid in ecological design, a handful of studies on Life Cycle Assessment (LCA) of hybrid electric vehicles (HEVs) and battery electric vehicles (BEVs) have been conducted in recent years.

The SUBAT project was the first study carried out to identify the most environment-benign battery intended for electric and hybrid electric vehicles.[1] Zackrisson *et al* applied LCA to batteries for plug-in hybrid electric vehicles (PHEVs). [2] Majeau-Bettez *et al* investigated the environmental footprint of lithium-ion and NiMH batteries for PHEVs and BEVs.[3] Notter *et al* looked at a BEV powered by lithium ion battery (LIB) and compared it against a similar ICEV.[4]

The SUBAT project and Zackrisson *et al* both found LIBs to be the more environment-friendly power source for electric vehicles. Notter *et al* pointed out that use phase was the single largest contributor of the total life cycle environmental impacts of BEVs, which was in agreement with the conclusion of Zackrisson *et al.* Notter *et al* also identified copper used as collector foil in anode as a hot spot in the production phase, while Majeau-Bettez *et al* found out the significance of nickel with regard to impact categories of ecotoxicity, acidification potential and abiotic depletion potential.

Different chemistries of cathode materials have been explored in the aforementioned studies. Zackrisson *et al* examine two LIBs based on a $LiFePO_4$ (LFP) cathode with different solvents for electrolytes. Majeau-Bettez *et al* investigated LIBs based on nickel cobalt manganese (NCM) and LFP respectively. Notter *et al* focused on a $LiMn_2O_4$ (LMO) -based LIB. However, there is no integrated life cycle comparison conducted on LIBs based on different cathode chemistries so far.

Besides interests in the life cycle impacts of BEVs, a few studies were focused on identifying the factors which could considerably affect the use phase environmental footprints of BEVs. Ma *et al*[5] and Faria *et al*[6] both found the driving profile of BEVs to be influential in the use phase GHG emissions and energy consumptions. Faria *et al* and Richardson[7] pointed out that the environmental friendliness of the electricity mix would largely determine the use phase impacts of BEVs. Ma *et al* also concluded that the marginal electricity to meet the BEV requirement was especially crucial to a greener transportation mode by BEVs. Nonetheless, despite existing studies aimed to improve the environmental performances of BEVs, the electrochemical properties of the LIB and its impact on the use phase impact remained unexamined.

In chapter 2, it was determined that active cathode materials were the most important contributor to the manufacturing phase environmental impacts of LIB, while anode and electrolyte materials played a minor role. Also, different active cathode materials can result in differences in power, energy density and cycling performance of batteries and therefore affect the use phase environmental burdens of BEVs[8], in our analysis we tried to fill the research gap and chose to study different cathode chemistries that are commercially available for LIBs. Special attention has been paid to the variability of electrochemical properties of active cathode materials and its impact on the environmental performances of BEVs. In addition to the active cathode material life cycle comparison, a systematic comparison of BEVs against ICEVs for different countries of different electricity mix is also nonexistent. In this paper we examined the environmental burdens of BEVs versus ICEVs for a few countries of representative electricity mix. This study aims to provide insights from a life-cycle perspective into possible improvement opportunities of LIB technology for BEVs, and identify countries as possible candidates who would benefit from a switch from ICEV dominated fleet to a BEV dominated one, given current vehicle technologies and electricity mix.

3.2 Methodology

Following the operation guide based on ISO standards[9], a streamlined life cycle approach is employed in this study, with the focus on the major life cycle stages of a mid-sized passenger BEV, which begin with raw material extraction and end with the full delivery of 120,000 miles. The cut-off criteria is set to be 1%, so end-of-life of the materials involved in the manufacturing and assembly process is not considered due to their relatively small contribution to the total environmental impacts. For the same reason, the LCA of machineries and vehicles used for transportation involved in the manufacturing and assembly process is not included in this work, while the machinery consumptions of electricity and natural gas, as well as the freighter consumptions of fuel are incorporated. Transportations of materials are calculated based on Ecoinvent standard transport distance for chemicals and metals. The functional unit is defined to be 120,000 miles traveled over a 10-year lifetime.

Among the five cathode chemistries studied in chapter 2, $LiCoO_2$ is more prevalent in LIBs for electronics, LMO and LFP are currently used in LIBs for BEV applications. Besides LMO and LFP, NCM, which can be considered as a combination of $LiNiMnO_4$ and $LiCoMnO_4$ modeled in chapter 2, is also a promising active cathode chemistry for LIBs used in BEVs and is likely to become the major player in the active cathode material for future LIBs. Therefore, the active cathode materials examined in this chapter include LMO, LFP and NCM. A $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ composition was assumed for the NCM material. NCM was prepared using coprecipitation method followed by calcination, while the synthesis method of LFP was assumed to be calcination. Each preparation pathway is approximated by corresponding laboratory synthesis method reported in literature, [10-14] assuming 95% yield. Material and energy inputs are obtained from Ecoinvent 2.0 database[15] due to better data availability. Energy consumptions of major production steps such as sintering and drying are estimated by the average of comparable industrial processes.[16] Materials inputs that are not found in Ecoinvent database are either substituted by similar chemicals, or synthesized according to industrially available method[17] using existing materials in the database.

Once the life cycle inventories (LCIs) of the materials of different battery components are in place, the LCI of a single LIB cell was constructed. As different literature[3, 4, 8, 18] published different material compositions for LIB cells, Battery Design Studio (BDS) was employed to generate a detailed and representative material composition of a single LIB cell. A sensitivity analysis was first conducted on a sample cell in the BDS database to test the dependence of cell performances on different cell design parameters. The results of the sensitivity analysis revealed that the performances of a single LIB cell, including energy density and capacity, were mainly determined by the design specifications such as loading of electrodes, stoichiometry of electrodes and jellyroll diameter, while variations in material composition of active materials had marginal impacts on the cell performances. Therefore, the material composition of the he18650 cell in the BDS database, which fell in the range of LIB cell material composition reported in aforementioned literature, was adapted to represent the LCI of a single LIB cell.

The material inputs for the LIB pack excluding LIB cell were obtained from Majeau-Bettez *et al* [3] and Notter *et a l*[4], and the energy input was approximated by the electricity and natural gas consumption by the dry room operation and the formation process.[18] The battery packs were assumed to have a total size of 40 kWh, according to the goals for advanced batteries for BEVs set by the United States Advanced Battery Consortium (USABC).[19] Over the lifetime of the BEVs, USABC also required that the LIBs should undergo at least 1,000 charge/discharge cycles.[20] Based on the cycle life provided by different LIB packs, replacement of LIB packs may be necessary. For the energy efficiencies, it's assumed that battery packs underwent linear degradation over its cycle life, and at the end of cycle life, they were 80% efficient.

Average values of energy density in Wh/kg and cycle life for different cathode materials published in literature[10-14, 20-33] and battery manufacturers[34-36] were determined. Electricity consumption of the use phase of BEV was subsequently calculated using Vehicle Simulation Program (VSP) [37], assuming European standard driving cycle, a depth of discharge of 80% and a charging loss of 10%. Recycling of BEVs and ICEVs, as well as secondary use of retired LIB's was not incorporated at this point, so that the environmental footprints obtained should be considered as the maximum possible values. During the life cycle impact assessment (LCIA) phase, the environmental impacts were evaluated by Ecoindicator 99 (EI99) with the hierarchic perspective and average weighting[38] in single score, Cumulative Energy Demand (CED) v

1.07and IPCC 2007 100-year Global Warming Potential (GWP) respectively. The assessment was done in SimaPro 7.2. Detailed information of the life cycle modeling is available in the supporting information.

To examine the impact of electrochemical properties of the active cathode materials, the environmental scores for 1 kWh of U.S. electricity, 1 liter of U.S. gasoline, LIB pack, and vehicle excluding battery pack were imported into MATLAB. In MATLAB, a range for possible energy density and cycle life was specified respectively. Then the total life cycle environmental impacts of a BEV with each specific combination of possible value of energy density and cycle life were calculated. After that, the environmental impacts of BEVs were compared with that of an ICEV, and the relative differences in environmental impacts between BEVs and an ICEV were plotted for each of the three cathode material-based BEVs.

To explore the sensitivity of the environmental performance of BEVs to electricity mix, life cycle comparison of BEVs against ICEVs were conducted for six countries: Brazil, China, France, Germany, India and the U.S. Electricity generation data were obtained from literature[39-46], and information on fuel economy and emissions of ICEVs in these countries were taken from various sources.[47-57] To account for the uncertainties in the specification of the two crucial parameter of a battery pack, Monte Carlo Simulation was also performed in MATLAB with 10,000 random samplings of the energy density and cycle life based on statistical distributions derived from collected values[10-14, 20-36] to present the common possible performance metrics of real-world battery packs used on BEVs. For each sampling, the differences in environmental impacts expressed by EI99 score, CED and GWP between BEV and ICEV were documented. In the end, probabilities of BEVs outperforming ICEVs based on the three environmental impacts indicators were calculated from the statistical analysis of the results of 10,000 samplings. The details of the stochastic modeling were documented in the supporting information.

3.3 Results and Discussions

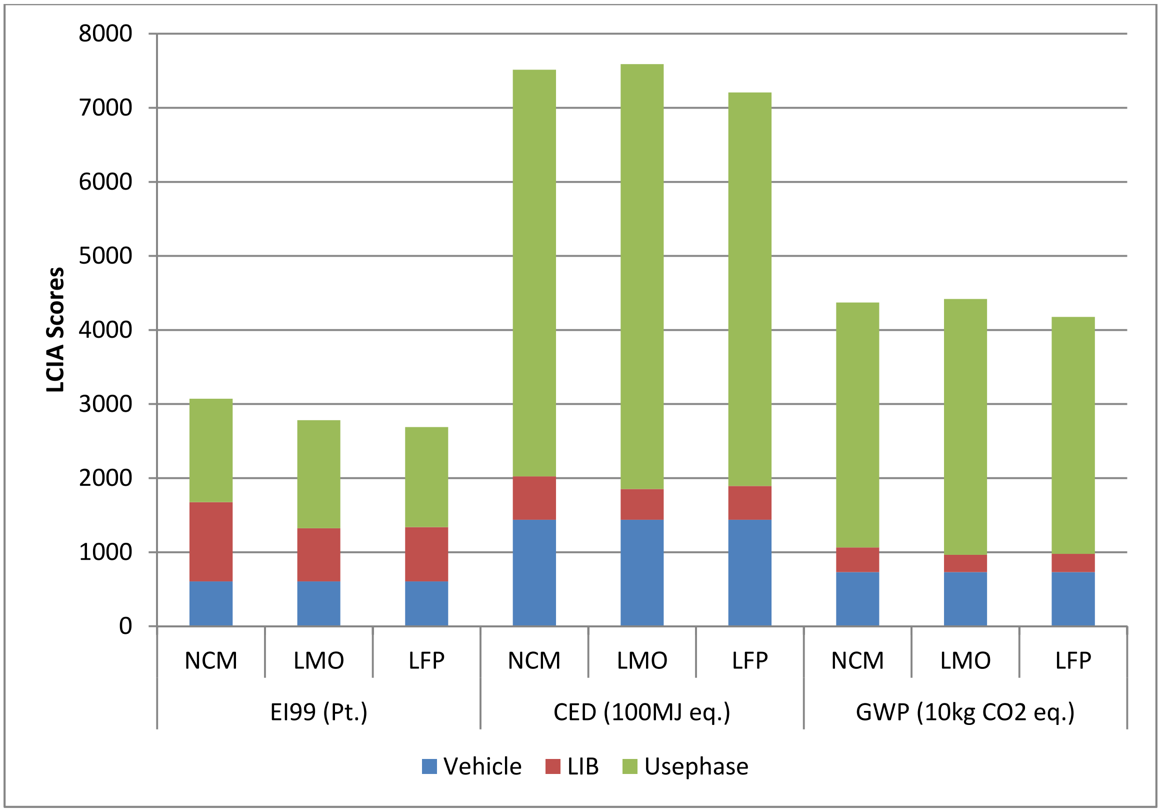

Figure 3-1. Life cycle comparison of BEVs across different cathode chemistries

The results of the comparison of the environmental impacts across different cathode chemistries of U.S. BEVs were shown in Figure 3-1. It is in consensus with the conclusions of other studies [3, 4] that use phase is the single largest contributor to the total life cycle environmental burden of BEVs, whose overall contributions range from 45.5% to 78.2%. The predominance is most evident in the impact categories of CED and GWP. LIB packs account for a substantial portion of the total environmental burden as well. The NCM pack represents 34.8% of the life cycle EI99 single score. For the LIB pack, active electrode materials are the most important environmental impact inducer, especially for NCM, where cadmium emission from the mining of nickel causes significant damages to the environment in terms of carcinogens and respiratory inorganics. Metal use for current collectors and casings of the LIB cell and the pack is also a remarkable source for the environmental footprints. Energy consumptions incurred during the manufacturing and the assembly phase, although not an outstanding contributor, account for up to 9% of the environmental burdens pertaining to the LIB pack.

The importance of the use phase in the life cycle modeling of BEVs justifies the value of the investigation into electrochemical properties of different LIB packs. The sensitivity of the environmental performances of BEVs to the electrochemical properties was presented in Figure 3-2. It can be observed that if the cathode material has a cycle life and energy density higher than the average value, BEVs always outperform ICEVs with regard to environmental impacts. For all of the three active cathode material-based LIB's, increases in energy density and cycle life all lead to decreases in environmental burdens of BEVs. When comparing the influences on the environmental performances of BEVs, cycle life of cathode materials seems to be of greater importance than energy density. For example, retaining an energy density of 115 Wh/kg, a small increase in cycle life from 999 to 1001 effectively tilts the environmental benefits to the LMO-based BEVs, which started as 3.0% less environmental beneficial than an ICEV, and ended up as 2.1% more environmental favorable than an ICEV in terms of GWP. This is because energy density only affects the average energy efficiency of a battery pack, while cycle life also affects number of battery pack needed in addition to average energy efficiency. A cycle life of 1000 serves as the dividing crest where the number of battery packs needed drops from 2 to 1.

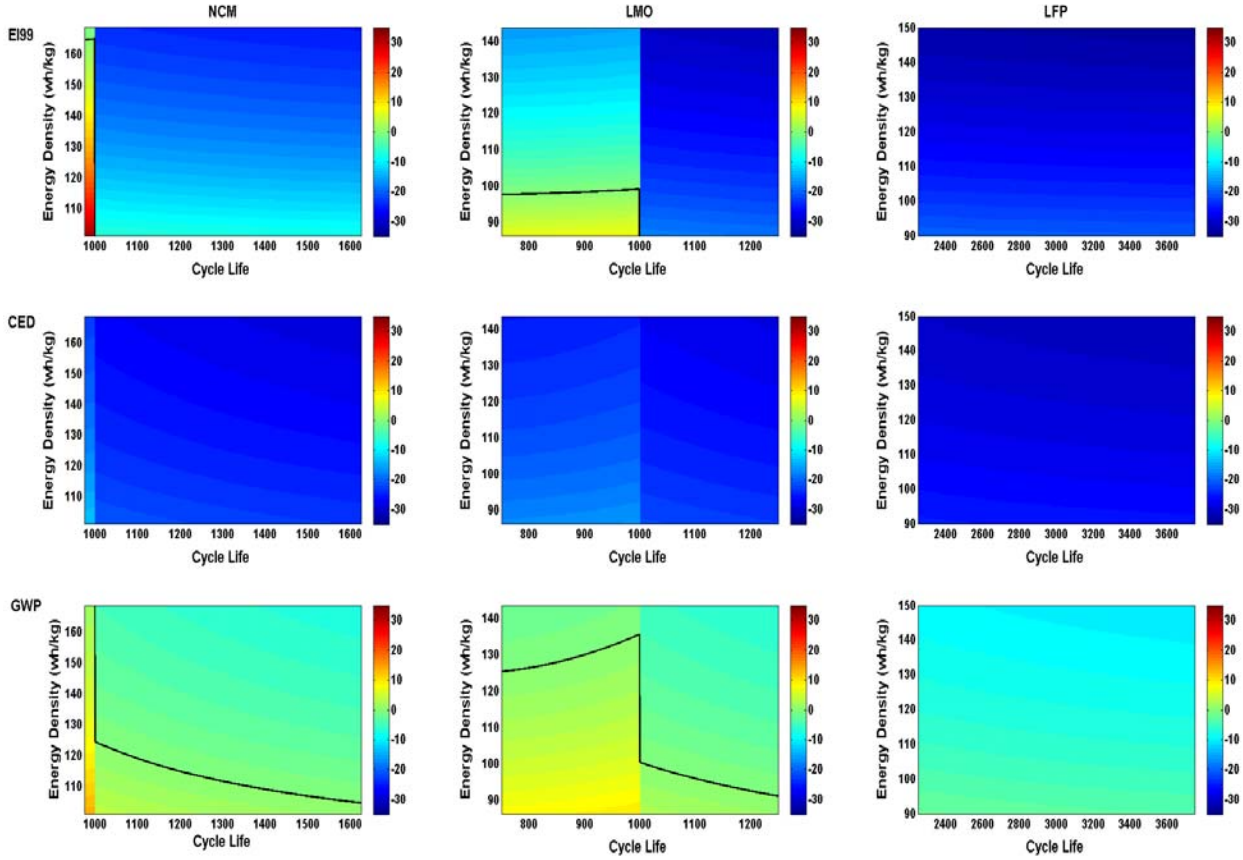

Figure 3-2.Relative changes of environmental impacts of BEV versus ICEV respond to changes of cycle life and energy density. The black line indicates where the BEV and ICEV exert the same environmental impact.

If different cathode materials were to be compared, LFP ranks first with respect to environmental friendliness among the three cathode materials for BEVs, mainly because its superior cycling performance eliminates the necessity to replace batteries during the lifetime of the vehicle, and partly due to the lower energy and material requirement pertaining to the manufacturing of the cathode material. NCM is more energy intensive to produce, and the cadmium emission from the extraction of nickel is a big environmental concern, however, the higher energy density of NCM causes a 4.3% reduction in the electricity consumption of BEVs in the use phase compared with the case of LMO, and the slightly improved cycle life makes NCM pack replacement less likely than LMO packs. Therefore, NCM-based LIBs outperforms LMO-based LIBs across all impact categories.

To examine the sensitivity of the results to the assumption of end-of life efficiency of LIBs, a scenario is constructed where LIBs are replaced when their efficiency reduce to 70% other than 80%. The results indicate better environmental performances in cases where replacement of LIBs are necessary, as the possibility of battery replacement decreases due to lower replacement criteria. However, this is achieved at the cost of lower average battery efficiency, which translates into higher per mile electricity consumption, and eventually leads to increase in the environmental impacts resulted from the use phase.

The results of the Monte Carlo Simulation were summarized in Figure 3-3. Monte Carlo simulation results for the six countries point to Brazil as the biggest potential beneficiary from a transformation to a BEV-dominated fleet. It's almost 100% sure that BEVs would outperform ICEVs despite variations in cathode chemistries and their electrochemical performances. It’s because 84% of electricity in Brazil is generated from hydropower, which is a renewable resource and low in CO_2 emission. France, who produces 76% of electricity from nuclear power, is also one of the top candidates for adoptions of BEVs other than the impact category of CED, as nuclear power is considered to be energy intensive. U.S. could also benefit from the adoption of BEVs if the battery could undergo at least 1000 charge-discharge cycles before it’s needed to be replaced. Germany, whose electricity mix is similar to that of the U.S., is also a place where the outlook of BEVs could be optimistic from an environmental perspective. However, the percentages of BEVs outperform ICEVs are slightly lower compared to the case in the U.S. due to the fact that ICEVs in Germany have higher fuel economy and comply to more stringent emission standards. For China and India, who rely heavily on coal for electricity generation, the adoption of BEVs appears to be less favorable than the case in the other four countries. In China, BEVs need to be based on LFP in order to be competitive with ICEVs across all environmental impact categories. In India, BEVs don't stand a chance to outperform ICEVs given current technology and conditions of electricity generation infrastructure. To further test the robustness of the result, a best technology scenario was constructed for India, where the thermal efficiency of the coal power plant was assumed to be the highest efficiency achieved by existing plant instead of the national average. The benefit of BEVs starts to emerge in the best technology scenario, which indicates that significant improvement in net energy conversion efficiency in electricity generation needs to be achieved if India anticipates environmental gains from BEV technologies.

Possible environmental reward of recycling was also investigated in this study. Hydrometallurgical, pyrometallurgical and intermediate physical recycling processes as described in literature[15, 55-56] were analyzed, with a focus on regeneration of metals and active cathode materials. Results of the recycling scenario suggest that recycling by hydrometallurgical process has the potential to reduce the manufacturing phase environmental impacts by 22%. It should be noted that however, current industrial-scale recycling, especially recycling of active material, only targets $LiCoO_2$-based LIBs, as manganese and iron have little economic value. Considerable effort is needed to develop recycling technologies that apply to other LIB cathode chemistries before environmental impact reduction can be achieved from recovered active cathode materials.

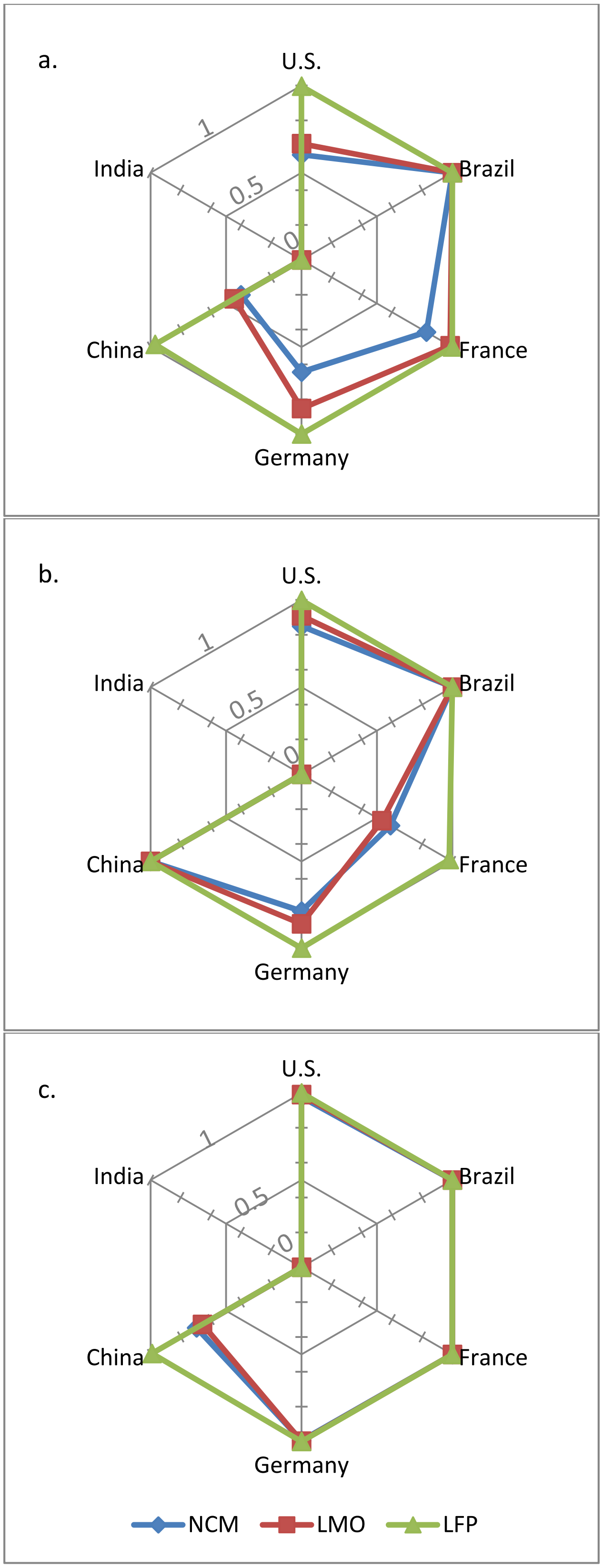

Figure 3-3. Percentages of BEVs outperforming ICEVs. a. EI99; b. CED; c. GWP

The findings of this study reveal that BEVs propelled by LIB's based-on common cathode materials, especially LFP, are very likely to be a greener mode of transportation than traditional ICEVs, regardless of substantial variations in performances of battery packs. Increasing the energy density and cycle life of the LIB, together with reductions in active electrode material and metal inputs would make BEVs–based transportation an even more environmental benign choice, so would a switch to a greener mix of electricity.

References

(1). Van Den Bossche, P.; Vergels, F.; Van Mierlo, J.; Matheys, J.; Van Autenboer, W. SUBAT: An assessment of sustainable battery technology. *J. Power Sources.* 2006, 162, 913–919.

(2). Zackrisson, M.; Avellan, L.; Orlenius, J. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles---critical issues. *J. Cleaner Production.* 2010, 18, 1519-1529.

(3). Majeau-Bettez, G.; Hawkins, T.R.; Stromman, A.H. Lief cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. *Environ. Sci. Technol.* 2011, 45, 4548-4554.

(4). Notter, D. A.; Gauch, M.; Widmer, R.; Wager, P.; Stamp, A.; Zah, R.; Althaus, H.-J. Contribution of Li-ion batteries to the environmental impact of electric vehicles. *Environ. Sci. Technol*. 2010, 44, 6550–6.

(5). Ma, H.R,; Balthasar, F.; Tait, N. A new comparison between the life cycle greenhouse gas emissions of battery electric vehicles and internal combustion vehicles. *Energ. Policy.* 2012, 44, 160-173.

(6). Faria, R.; Marques, P.; Moura, P. Impact of the electricity mix and use profile in the life-cycle assessment of electric vehicles. *Renewable Sustainable Energy Reviews.* 2013, 24, 271-287.

(7). Richardson, D.B. Electric vehicles and the electric grid: a review of modeling approaches, impacts and renewable energy integration. *Renewable Sustainable Energy Reviews.* 2013, 19, 247-254.

(8). Sullivan, J.L. and Gaines, L. *A review of battery life-cycle analysis: state of knowledge and critical needs.* Center for Transportation Research, Energy System Division, Argonne National Laboratory, Illinois, U.S., 2010.

(9). Guinee, Jeroen B. *Handbook of Life Cycle Assessment: Operation Guide to ISO standards*. Kluwer Academic Publishers: Dordrecht, Netherlands, 2002.

(10). Lee, M.H.; Kang, Y.J.; Myung, S.T.; Sun, Y.k.. Synthsis optimization of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ via co-precipitation. *Electrochimica Acta*. 2004, 50, 939-948.

(11). Todorov, Y.M.; Numata, K.. Effects of the Li: (Mn+Co+Ni) molar ratio on the electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material. *Electrochimica Acta*. 2004, 50, 495-499.

(12). Nukuda, T.; Inamasu, T.; Fujii, A.; Endo, D.; Nakagawa, H.; Kozono, S.; Iguchi, T.; Kuratomi, J.; Kohno, K.; Izuchi, S.; Oshitani, M.. Development of a lithium ion battery using a new cathode material. *J. Power Sources.*2005, 146, 611-616.

(13). Yamada, A.; Chung, S.C.; Hinokuma, K. Optimized $LiFePO_4$ for lithium battery cathodes. *J. Electrochem. Soc.* 2001, 148, A224-A229.

(14). Garcia-Moreno, O.; Alvarez-Vega, M.; Garcia-Alvarado, E.; Garcia-Jaca, J.; Gallardo-Amores, J.M.; Sanjuan, M.L.; Amador, U.. Influence of the structure on the electrochemical performance of lithium transition metal phosphates as cathodic materials in rechargeable lithium batteries: a new high-pressure form of $LiMPO_4$ (M=Fe and Ni). *Chem. Mater.* 2001, 13, 1570-1576.

(15). *Overview and Methodology*; ecoinvent report No. 1. Swiss Centre for Life Cycle Inventories: Dübendorf, Switzerland, 2007;

(16). Brown, H.L.; Hamel, B.B.; Hedman, B.A. *Energy Analysis of 108 Industrial Processes*. The Fairmont Press, Inc.: Upper Saddle River, NJ, 1996.

(17). *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA:

Weinheim, Germany, 2005.
(18). Dunn, J.B.; Gaines, L.; Barnes, M.; Sullivan, J.; Wang, M. *Material and energy flows in the materials production, assembly, and end-of-life stages of the automotive Lithium-ion battery life cycle*. Center for Transportation Research, Energy System Division, Argonne National Laboratory, Illinois, U.S., 2012.
(19). USABC Goals for Advanced Batteries for EV's, United States Council for Automotive Research LLC.
http://www.uscar.org/guest/article_view.php?articles_id=85
(20). Yi, T.F.; Hao, C.L.; Yue, C.B.; Zhu, R.S.; Shu, J. A literature review and test: structure and physicochemical properties of spinel $LiMn_2O_4$ synthesized by different temperatures for lithium ion battery. *Synthetic Met.* 2009, 159, 1255-1260.
(21). Liu, W.; Farrington, G.C.; Chaput, F.; Dunn, B. Synthesis and electrochemical studies of spinel phase $LiMn_2O_4$ cathode materials prepared by the Pechini process. *J. Electrochem. Soc.* 1996, 143, 879-884.
(22). Park, Y.J.; Lim, J.G.; Kim, M.K.; Chung, H.T.; Kim, H.G. Preparation of $LiMn_2O_4$ thin films by a sol-gel method. *Solid State Ionics.* 2000, 130, 203-214.
(23). Subramania, A.; Angayarkanni, N.; Vasudevan, T. Effect of PVA with various combustion fuels in sol-gel thermolysis process for the synthesis of $LiMn_2O_4$ nanoparticles for Li-ion batteries. *Mater. Chem. Phys.* 2007, 102, 19-23.
(24). Sun, Y.K.; Oh, I.H.; Kim, K.Y. Synthesis of spinel $LiMn_2O_4$ by the sol-gel method for a cathode-active material in lithium secondary batteries. *Ind. Eng. Chem. Res.* 1997, 36, 4839-4846.
(25). Li, T.; Qiu, W.H.; Zhao, R.H.; Xia H.; Zhao, H.L.; Liu, J.J. Effects of sintering time on the electrochemical properties of spinel $LiMn_2O_4$ synthesized by solid-state reaction. *J. Univ. Sci. Technol. B.* 2008, 15, 74-78.
(26). Takahashi, M.; Ohtsuka, H.; Akuto, K.; Sakurai, Y. Confirmation of long-term cyclability and high thermal stability of $LiFePO_4$ in prismatic lithium-ion cells. *J. Electrochem. Soc.* 2005, 152, A899-A904.
(27). Choi, D. and Kumta, P.N. Surfactant based sol-gel approach to nanostructured $LiFePO_4$ for high rate Li-ion batteries. *J. Power Sources.* 2007, 163, 1064-1069.
(28). Prosini, P.P.; Cianchi, L.; Spina, G.; Lisi, M.; Scaccia, S.; Carewska, M.; Minarini, C.; Pasquali, M. Synthesis and characterization of amorphous $3Fe_2O_3.2P_2O_5.10H_2O$ and its electrode performance in lithium batteries. *J. Electrochem. Soc.* 2001, 148, A1125-A1129.
(29). Xu, Z.H.; Xu, L.; Lai, Q.Y.; Ji, X.Y. A PEG assisted sol-gel synthesis of $LiFePO_4$ as cathodic material for lithium ion cells. *Mater. Res. Bull.* 2007, 42, 883-891.
(30). Doeff, M.M.; Hu, Y.Q.; McLarnon, F.; Kostecki, R. Effect of surface carbon structure on the electrochemical performance of $LiFePO_4$. *Electrochem. Solid St.* 2003, 6, A-207-A209.
(31). Jang, M.W.; Jung, H.G.; Scrosati, B.; Sun, Y.K.. Improved co-substituted, $LiNi_{0.5-x}Co_{2x}Mn_{1.5-x}O_4$ lithium ion battery cathode materials. *J. Power Sources.*2012, 220, 354-359.
(32). Omar, N.; Verbrugge, B.; Mulder, G.; Van den Bossche, P.; Van Mierlo, Joeri; Daowd, M.; Dhaens, M.; Pauwels, S.. Evaluation of performance characteristics of various lithium-ion batteries for use in BEV application. *Vehicle Power and Propulsion Conference (VPPC),* September 1-6, 2010.
(33). Hohne, K.; Hirtz, E.. With system integration and lightweight design to highest energy densities. *Advanced Microsystems for Automotive Application 2013*. Lecture Notes in Mobility 2013, 205-214.

(34). *Kokam Superior Lithium Polymer Battery (SLPB) Cell Specification Data*. Kokam Co. Ltd: Korea, 2009;
http://www.elektronik.ropla.eu/pdf/stock/kok/tech_spec_slpb120216216_53ah.pdf
(35). *Lithium Ion Battery.* LG Chem Power Inc.;
http://www.lgcpi.com/lithium.shtml
(36). *AMP 20 Prismatic Pouch Cell Data Sheet.* A123 System, Inc.;
http://www.a123systems.com/prismatic-cell-amp20.htm
(37). Mierlo, J.V. and Maggetto, G. Innovative iteration algorithm for a vechile simulation program. *IEEE T. Veh. Tech.* 2004, 53, 401-412.
(38). *The Eco-indicator 99 A Damage Oriented Method for Life Cycle Impace Assessment;* Methodology report. Pre Consultants B.V., Amersfoort, Netherlands, 2001;
http://www.pre.nl/download/misc/EI99_methodology_v3.pdf
(39). *Coal in the Energy Supply of India;* Coal Industry Advisory Board/International Energy Agency: Paris, France, 2002.
(40). *World Energy Outlook 2007: China and India Insight;* International Energy Agency: Paris, France, 2007.
(41). Chakraborty, N.; Mukherjee, I.; Santra, A.K.; Chowdhury, S.; Chakraborty, S.; Bhattacharya, S.; Mitra, A.P.; Sharma, C. Measurement of CO_2, CO, SO_2 and NO emissions from coal-based thermal power plants in India. *Atmos. Environ.* 2008, 42, 1073-1082.
(42). *Anthropogenic Emissions from Energy Activities in India*: Generation and Source Characterization, Program for Computational Reactive Mechanics (PCRM). Ohio Supercomputer Center;
http://www.osc.edu/research/archive/pcrm/emissions/thermalemissions.shtml
(43). *Report (Part-I) of the Expert Committee on Road Map for Coal Sector Reforms*; Ministry of Coal, Government of India: New Delhi, India, 2005;
http://www.coal.nic.in/expertreport.pdf
(44). *Country Analysis Briefs: India*. EIA;
http://www.eia.gov/countries/cab.cfm?fips=IN
(45). *Country Analysis Briefs: China*. EIA;
http://www.eia.gov/countries/cab.cfm?fips=CH
(46). *Country Analysis Briefs: Brazil*. EIA;
http://www.eia.gov/countries/cab.cfm?fips=BR
(47). *Average Fuel Efficiency of U.S. Light Duty Vehicles*. Research and Innovative Technology Administration, Bureau of Transportation Statistics;
http://www.bts.gov/publications/national_transportation_statistics/html/table_04_23.html
(48). *Light-Duty Vehicle, Light-Duty Truck, and Medium-Duty Passenger Vehicle – Tier 2 Exhaust Emission Standards.* US EPA;
http://www.epa.gov/oms/standards/light-duty/tier2stds.htm
(49). *Gasoline Sulfur Standards.* US EPA;
http://www.epa.gov/oms/standards/fuels/gas-sulfur.htm
(50). *Emission Norms.* Society of Indian Automobile Manufacturers;
http://www.siamindia.com/scripts/emission-standards.aspx
(51). Chugh, R.; Cropper, M.; Narain, U. The cost of fuel economy in the Indian passenger vehicle market. *Energ. Policy.* 2011, 39, 7174-7183.
(52). Huo, H.; Yao, Z.L.; He, K.B.; Yu, X. Fuel Consumption rates of passenger cars in China: Labels versus real-world. *Energ. Policy.* 2011, 39, 7130-7135.

(53). Wang, H.K.; Fu, L.X.; Bi, J. CO_2 and pollutant emissions from passenger cars in China. *Energ. Policy.* 2011, 39, 3005-3011.
(54). Schmitt, W.F.; Szklo, A.; Schaeffer, R. Policies for improving the efficiency of the Brazilian light-duty vehicle fleet and their implications for fuel use, greenhouse gas emissions and land use. *Energ. Policy.* 2011, 39, 2163-3176.
(55). Wills, W.; La Rovere, E.L. Light vehicle energy efficiency programs and their impact on Brazilian CO_2 emissions. *Energ. Policy.* 2010, 38, 6453-6462.
(56). *Brazilian Automotive Industry Yearbook 2011*; Brazilian Automotive Industry Association: Sao Paulo, Brazil, 2011.
(57). Salvo, A.; Huse, C. Build it, but will they come? Evidence from consumer choice between gasoline and sugarcane ethanol.
http://www.kellogg.northwestern.edu/faculty/salvo/htm/fuelchoice.pdf
(58). Dewulf, J.; Van der Vorst, G.; Denturck, K.; Van Langenhove, H.; Ghyoot, W.; Tytgat, J.; Vandeputte, K. Recycling rechargeable lithium ion batteries: critical analysis of natural resource savings. *Resour. Conserv. Recy.* 2010, 54, 229-234.
(59). Li, L.; Ge, J.; Wu, F.; Chen, R.J.; Chen, S.; Wu, B.R. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J. Hazard. Mater.* 2010, 176, 288-293.

3.4 Supporting Information

3.4.1 System boundary and descriptions

The system boundary of the study is depicted in Figure S3-1. The cut-off criteria is set to be 1%, suggesting processes and material/energy inputs whose contributions to the total environmental is less than 1% will not be included in the analysis.

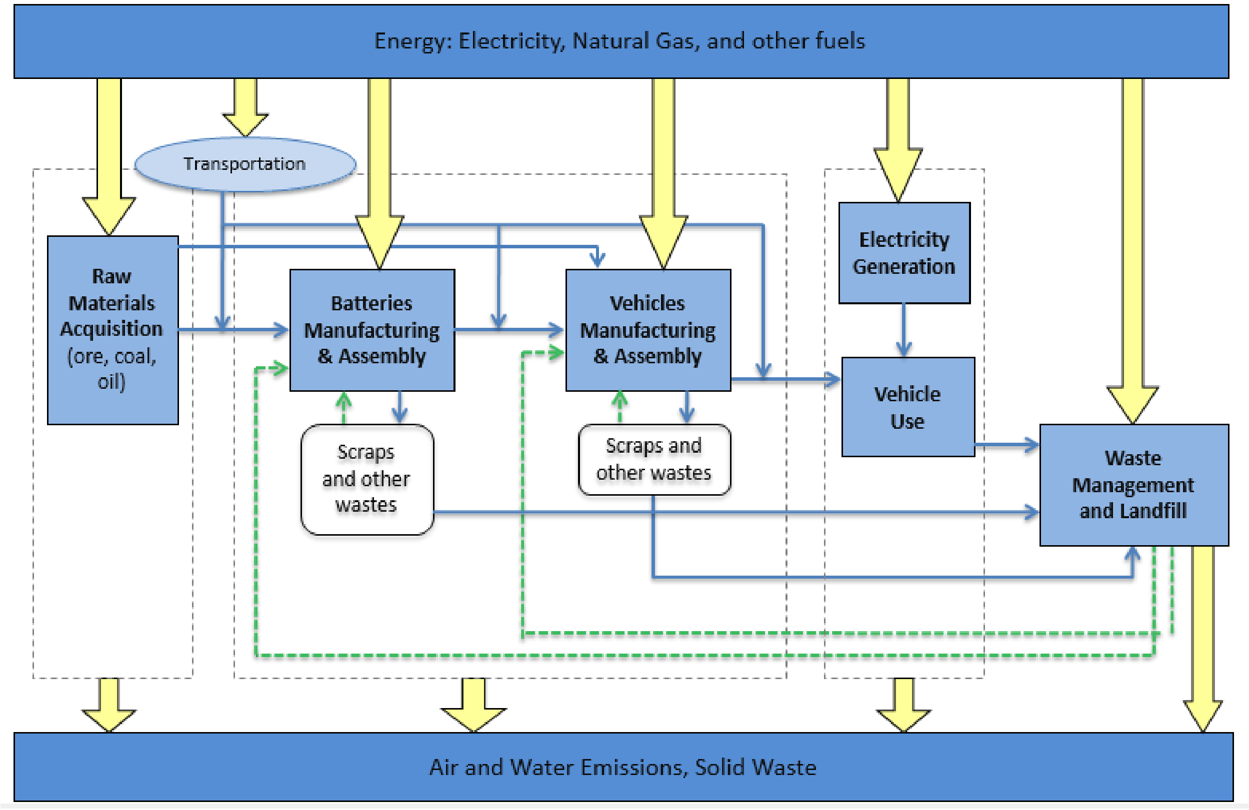

Figure S3-4. System boundary of the LCA study of BEVs

3.4.2 Manufacturing and Assembly of LIB

3.4.2.1 Active cathode material synthesis

LFP is assumed to be produced by calcination method as specified in 1 and 2. And the LCI of the synthesis is summarized in Table S3-1. For NCM, a composition of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is assumed due to better data availability. The synthesis of NCM starts with the preparation of the precursor of the active cathode materials by co-precipitation, and proceeds with calcination of the precursor and LiOH as described in 3-5. Table S3-2 and S3-3 give the LCI of the two processes respectively.

Table S3-3. LCI of LFP Synthesis

Products		
LiFePO4 calcination	1	kg
Materials input		
Fe(Ac)2	1.1589	kg
Acetone, liquid, at plant/RER U	0.1	Kg
Chemical plant, organics/RER/I U	4E-10	p
Mono-ammonium Phosphate	0.916	kg
Electricity, medium voltage, at grid/CN U	0.005	kWh
Lithium carbonate, at plant/GLO U	0.2463	kg
Energy inputs		
Transport, freight, rail/RER U	1.453	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	27.674	MJ
Transport, lorry >16t, fleet average/RER U	0.242	tkm
Electricity, medium voltage, at grid/CN U	0.005	kWh
Emissions to air		
Carbon dioxide, fossil	0.1465	kg
Heat, waste	0.018	MJ

Table S3-4. LCI of NCM precursor preparation

Products		
Ni1/3Co1/3Mn1/3(OH)2	1	kg
Materials inputs		
MnSO4 2M solution	5.746	l
NiSO4 2M solution	5.746	l
CoSO4 2M solution	5.746	l
Sodium hydroxide 6M solution	3.829	l
Ammonia aqueous solution, saturated	1	l
Water, deionised, at plant/CH U	1	kg
Energy inputs		
Heat, natural gas, at industrial furnace >100kW/RER U	0.232	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh

3.4.2.2 LIB single cell manufacturing

LIB single cell inventory is obtained from BDS and is listed in Table S-4. For different LIBs based on different cathode chemistries, the only difference exists in the active cathode materials, while materials for other battery components stay invariant.

Table S3-5. LCI of NCM synthesis

Products		
NCM, co-precipitation	1	kg
Materials inputs		
Lithium hydroxide, at plant/GLO U	0.2615	kg
Ni1/3Co1/3Mn1/3(OH)2	0.9982	kg
Oxygen, liquid, at plant/RER U	0.0872	kg
Energy inputs		
Electricity, medium voltage, at grid/CN U	0.005	kWh
Heat, natural gas, at industrial furnace >100kW/RER U	21.388	MJ
Transport, freight, rail/RER U	0.7733	tkm
Transport, lorry >16t, fleet average/RER U	0.1347	tkm

Table S3-6. LCI of LIB single cell

Products		
LIB single cell	1	p
Materials inputs		
Active cathode material	12.3942	g
Graphite, battery grade, at plant/CN U	8.0976	g
Lithium hexafluorophosphate, at plant/CN U	0.6762	g
Carbon black, at plant/GLO U	0.6825	g
Ethylene carbonate, at plant/CN U	4.3344	g
Polyvinylfluoride film, at plant/US U	1.1823	g
Polyethylene terephthalate, granulate, bottle grade, at plant/RER U	0.441	g
Polyethylene, LDPE, granulate, at plant/RER U	0.7287	g
Steel, electric, chromium steel 18/8, at plant/RER U	9.03	g
Cathode, copper, primary copper production/GLO U	3.62565	g
Aluminium, primary, at plant/RER U	1.77975	g
Energy inputs		
Transport, freight, rail/RER U	0.0191	tkm
Transport, lorry >16t, fleet average/RER U	0.0043	tkm

3.4.2.3 LIB pack assembly

The material inputs for the assembly of LIB packs from LIB single cells were obtained from 6 and 7. Dunn *et al* estimated an energy consumption of 2.3 mmBtu/ton battery for the assembly phase, with energy requirement of dry room operation as the single largest contributor.[8] In this study, the energy inputs were approximated by the electricity and natural gas consumption by the dry room operation and the formation process.

The manufacturing of Li EV batteries requires a dry room for certain processes during their assembly. Life cycle inventory of the dry room were based on a dimension of 50 mx20 mx6 m. The estimate of dimension was based on the surface area and layout of completed projects (including the dry room for LG Chem and A123 System) by the manufacturer.[9]

Electricity and natural gas consumption of dry room operation, equal to 0.0088kWh/cell and 0.058MJ/cell respectively, were estimated based on annual consumption provided by the dry room manufacturer.[10] The formation cycling process was represented by one formation cycle and three additional cycles, and the corresponding energy consumption were estimated to be 0.0005kWh/cell. It was assumed that dry room operation and formation cycling accounts for 60% of the electricity consumption of the manufacturing facility.

Table S3-7. LCI of dry room

Cladding, crossbar-pole, aluminium, at plant/RER U	3680	m2
Polyvinylfluoride, at plant/US U	4600	kg
Ventilation system, central, 1 x 720 m3/h, PE ducts, with GHE/CH/I U	1	p
Concrete, sole plate and foundation, at plant/CH U	300	m3
Transport, lorry >16t, fleet average/RER U	97700	tkm
Electricity, medium voltage, at grid/US U	10500	kWh
Polystyrene foam slab, at plant/RER U	9936	kg
Heat pump 30kW/RER/I U	3	p

3.4.3 Modeling of use phase

The mass of the battery pack for a typical passenger BEV needs to be determined before analysis can be done on the pack-scale. Since LCA studies comparing different products should be based on the assumption that these products provide the same function, one measurement of function provided by the battery pack should be kept invariant in the comparison of LIBs with different cathode materials. The most intuitive function would be the range delivered by the battery pack. However, as there were great uncertainties in the ranges provided by different commercially-available BEVs as well as ranges projected for future BEVs, and the range of BEVs could not be explicitly related to battery mass, which would involve the modeling of driving behavior, total pack size in kWh was selected as the key function restraint. It thereby enabled a direct calculation of battery mass from energy density, and would not be subjected to significant change in the near future.

Table S3-8. LCI of LIB cell assembly into LIB pack

Products		
cell assembly, U/US	1	p
Materials inputs		
Integrated circuit, IC, logic type, at plant/GLO U	0.01	g
Water, deionised, at plant/CH U	6.707	g
Aluminium, primary, at plant/RER U	7.2	g
Nickel, 99.5%, at plant/GLO U	0.045	g
Cable, data cable in infrastructure, at plant/GLO U	0.018	m
Steel, electric, chromium steel 18/8, at plant/RER U	0.1	g
Energy inputs		
Electricity, medium voltage, at grid/US U	0.015	kWh
Natural gas, burned in industrial furnace >100kW/RER U	0.07	MJ
Sheet rolling, aluminium/RER U	8.97975	g
Sheet rolling, copper/RER U	3.62565	g
Sheet rolling, chromium steel/RER U	9.03	g
Injection moulding/RER U	1.1697	g
Transport, lorry >16t, fleet average/RER U	0.0014	tkm
Transport, freight, rail/RER U	0.0056	tkm

Average values of energy density in Wh/kg and cycle life for different cathode materials published in literature and battery manufacturers were selected, as shown in Table S3-7, with statistical distributions derived from collected values to present the common possible values of real-world battery packs used on BEVs. Battery mass was therefore determined as the total size divided by energy density, and then the number of single LIB cells for a battery pack could be readily calculated.

Table S3-9. Electrochemical properties of LIBs based on different cathode chemistries

		NCM[3-5, 11-13]	LMO[14-21]	LFP[1, 2, 22-27]
Energy Density (Wh/kg)	Distribution	Normal	Normal	Normal
	Mean	135	115	120
	Variance	400	400	400
Cycle Life	Distribution	Lognormal	Lognormal	Lognormal
	Mean	1300	1000	3000
	Variance	600	200	600

Using the subsequent calculation, range delivered by a BEV was determined as

$$Range = \frac{DOD * E * M * \eta}{M * \alpha + \beta}$$

where DOD is depth of discharge and was assumed to be 80% in this study; E is energy density of a specific LIB cell; M is the corresponding battery mass; η is the corresponding average energy efficiency; α and β are energy coefficients derived from Vehicle Simulation Program (VSP) [1], which accounts for the additional energy required to haul the battery pack. From the predefined function of 120,000 miles driven of BEVs, together with the average range and cycle life provided by a specific battery pack, the number of battery packs needed could be determined, so did the environmental impacts resulted from the manufacturing of battery packs. For the vehicle parts excluding battery pack, BEVs were assumed to have the same configuration as ICEVs, and the LCI for these parts, including glider and drivetrain were adapted from the ICEV inventory reported by Notter *et al.*[4] Regarding the use phase, assuming 10% charging loss, electricity consumption per mile driven for a BEV was readily calculated from range and total pack size.

3.4.4 Recycling scenario analysis of spent LIBs

Three recycling methods were investigated for spent LIBs in this study, including hydrometallurgical process, pyrometallurgical process and intermediate physical recycling process, among which the pyrometallurgical and physical recycling processes are already deployed in commercial operation, while the hydrometallurgical process is still under development. [8] LCI for each recycling process was listed in Table S3-8~3-10.

Table S3-10. LCI of recycling 1 kg spent LIB by hydrometallurgical process

Material inputs		
	Value	Unit
Spent LIB	1	kg
NMP	0.14	g
Citric acid	0.952	kg
H2O2	0.174	kg
water	1.2	kg
Energy inputs		
	Value	Unit
Electricity	0.351	kWh
Natural gas	1.485	MJ
Transportation, rail	3.152484	tkm
Transportation, road	0.525414	tkm
Material outputs		
	Value	Unit
Lithium citrate	0.485	kg
Cobalt citrate	0.972	kg
Graphite	64	g
Aluminum	75.6	g
Copper	31	g
Steel	126	g
Emissions		
	Value	Unit
CO2	85.4	g

Table S3-11. LCI of recycling 1 kg spent LIB by pyrometallurgical process

Material input		
	Value	Unit
Coke	0.09	kg
CaO	0.129	kg
air	1.042	kg
Water vapor	1.83	kg
cooling water	0	kg
H2SO4	0.535118	kg
HCl	223.4694	g
H2O2	62.44898	g
Energy input		

Electricity	0.565	kWh
Natural gas	0.534	MJ
Transportation, rail	181.1143	tkm
Transportation, lorry	30.18571	tkm
Material output		
EC	68.8	g
CuSO4	78.41372	g
FeSO4	343.14	g
Co3O4	177.0612	g
Emissions		
CO2	1.071731	kg

Table S3-12. LCI of recycling 1 kg spent LIB by intermediate physical process

Material inputs		
	Value	Unit
Spent LIB	1	kg
Liquid nitrogen	0.808	kg
water	1.2	kg
Soda ash	14.3	g
Energy inputs		
	Value	Unit
Electricity	0.49	kWh
Transportation, rail	1.813	tkm
Transportation, road	0.302167	tkm
Material outputs		
	Value	Unit
Lithium carbonate	8.79	g
Aluminum	75.6	g
Copper	31	g
Steel	126	g

3.4.5 Modeling of sensitivity to changes in electrochemical properties

A range of ±25% of the average energy density and cycle life was assumed for each cathode chemistry. Sample MATLAB code to model sensitivity to electrochemical properties is as follows.

```
%This program plots the environmental performances of BEV(LFP cathode) vs.
%ICEV based on differences in energy density and cycle life of cathode
%material.

clear all
format short

%Changing values
energy_density=(120*0.75:0.25:120*1.25);%Median=120Whr/kg
cycle_life=(3000*0.75:3:3000*1.25);%Median=3000

%Fixed values
DOD=0.8;
alpha=0.054;%VSP energy coefficient
beta=133;%VSP energy coefficient
charging_loss=0.1;
required_cycle=1000;%Based on ABC standard
W_singlecell=0.05;%Single cell weight
EI_singlecell=0.1099;%EI99 points of calcination LFP
EI_others=605.5;%EI99 points of EV excluding battery
EI_perkwh=0.0326;%EI99 points of 1 kwh electricity at US grid
EI_perliter=0.1902;%EI99 points of 1 liter gasoline
ICEV_fuele=0.1377;%Fuel economy of ICEV in liter per mile

%Environmental impact of ICEV
ICEV=615.5+EI_perliter*ICEV_fuele*120000;

EV_outperform=zeros(length(energy_density),length(cycle_life));
EI_diff=zeros(length(energy_density),length(cycle_life));
EI_EV=zeros(length(cycle_life)*length(energy_density),11);
num=1;

%Assume a totoal battery pack size of 40kwh based on ABC standard.
for i=1:length(energy_density)
    clear Bat_mass N_cell
    Bat_mass=40/energy_density(i)*1000;
    N_cell=ceil(Bat_mass/W_singlecell);
    for j=1:length(cycle_life)
        clear N-bat eff_last energy_efficiency range elec_con EI comp
        N_bat=ceil(required_cycle/cycle_life(j));
        %Final efficiency of the last functional battery pack
        eff_last=1-rem(required_cycle,cycle_life(j))*0.2/cycle_life(j);
        %Average energy efficiency of all battery packs
        energy_efficiency=1-(0.2*cycle_life(j)*fix(required_cycle/cycle_life(j))...
            +(1-eff_last)*rem(required_cycle,cycle_life(j)))/(2*required_cycle);
        %Range
        range=DOD*energy_density(i)*Bat_mass*energy_efficiency/(Bat_mass...
            *alpha+beta)*0.6213712;
        %Electricity consumption in kwh/mile
        elec_con=40*(1+charging_loss)/range;

        %Calculate environmnetal burden of EV
        EI=EI_singlecell*N_cell*N_bat+EI_others+EI_perkwh*elec_con*120000;
```

```
        EI_diff(i,j)=(EI-ICEV)/ICEV*100;

        %Compare environmnetal imapcts of EI and ICE
        if(EI<ICEV)
            comp=0;
        else comp=1;
        end
        EV_outperform(i,j)=comp;

        %Write output into EI_EV matrix
        EI_EV(num,1)=energy_density(i);
        EI_EV(num,2)=cycle_life(j);
        EI_EV(num,3)=Bat_mass;
        EI_EV(num,4)=N_cell;
        EI_EV(num,5)=N_bat;
        EI_EV(num,6)=energy_efficiency;
        EI_EV(num,7)=range;
        EI_EV(num,8)=elec_con;
        EI_EV(num,9)=EI;
        EI_EV(num,10)=comp;

        num=num+1;
    end
end

clf
figure(1)
h=pcolor(cycle_life,energy_density,EV_outperform);
set(h,'EdgeColor','none');%Controls grid
axis tight;
xlabel('Cycle Life');
ylabel('Energy Density (wh/kg)');
title('Occurrence of EV (LiFePO4) Outperforming ICEV Based on EI99');

figure(2)
pcolor(cycle_life,energy_density,EI_diff);
shading flat;%Delete this line to show grid
colorbar('location','eastoutside');
axis tight
xlabel('Cycle Life');
ylabel('Energy Density (wh/kg)');
```

3.4.6 Monte Carlo Simulation

3.4.6.1 Modeling Indian power generation

The electricity mix of India was obtained from IEA.[28] Since India's electricity is mostly generated from coal, LCI for coal power representing the case in India was constructed, while for electricity generation by other sources, same values as the LCI inventory of China electricity were assumed. The transportation distance for coal was estimated to be 500 km, [29] and a caloric value of 15 MJ/kg was assumed for Indian coal.[30] Major criteria pollutants emissions for India coal power[31] were summarized in Table S3-11. Other emissions were assumed to be the same as the case of China. Average thermal efficiency for coal power plants was 26.5% according to IEA. [32] For transmission loss and relevant emissions, it's assumed to be the same as the case of Swiss, in order to be consistent with LCI of electricity generation for other countries that are available in the Ecoinvent database. For the best technology scenario, data of the Singrauli Power Station, which is the most efficient plant among those with a capacity great than 2000 MW was used. The thermal efficiency is increased to 36%, the coal feed rate is reduced to 0.61 kg/kWh, and major criteria pollutants emissions also decrease. [30]

Table S3-13. Emission to air from generation of 1kWh electricity in Indian coal power plant

Species	Emissions	Unit
CO2	0.998	kg
CO	3.393	g
SO2	8.696	g
NO	2.42	g

3.4.6.2 Life cycle modeling of ICEVs use phase in six countries

To model the use phase of BEVs, LCIs for gasoline in those countries excluding Germany and France need to be constructed first. For U.S. gasoline, the LCI of gasoline at the refinery was taken from the USLCI database, while the material and energy inputs from the refinery to regional storage were assumed to be the same as the case of European average. For Brazil, China and India, oil production mix data were taken from IEA, [33-35] and LCIs of gasoline for those three countries were constructed to reflect the actually production mix, while the refinery condition and emissions from refinery, further processing from unleaded gasoline to low sulfur gasoline and domestic transportation and distribution were assumed to be the same as European average due to difficulties in obtaining data exclusive to those countries.

Table S3-14. Summary of ICEV FE and Emissions

	FE (kg.km)	Emissions (g/km)				
		CO2	CO	HC	NOX	PM10
Brazil[38-41]	0.01969 ethanol,	111.16	2	0.3	0.12	0.025

	0.04464 gasoline					
China[42-43]	0.064917	230	5.36	0.71	0.49	0.021
India[44-45]	0.05745	190.03	3.88	0.25	0.18	N/A

For the operation of ICEVs, 2010 European fleet average was assumed for Germany and France. For the U.S., it's assumed that the ICEV meets the CAFÉ standards for 2010[36] and the EPA tier 2 emission standards.[37] For Brazil, China and India, fuel economy (FE) and vehicle emissions were collected from literature. For emissions that are not available from literature, Brazilian and Chinese ICEVs were assumed to have the same emissions as European vehicles meeting Euro4 emission standard, while Indian ICEVs were equivalent to European vehicles meeting Euro3 emission standards. The composite FE and emissions results were summarized in Table S3-12. It should be noted that for Brazil, the fleet is dominated by flex fuel vehicles, which can run on both gasoline and pure ethanol. The weighted fuel consumption mix for 2010 Brazilian fleet average is calculated to be 22.46% share of pure ethanol based on the finding of a study of the choice of fuels by drivers of flex fuel vehicles.[41] Sample MATLAB code for Monte Carlo Simulation is as follows.

```
clear all
format short

N_simu=100000;%Number of simulation

%Calculate parameters of normal distribution_Energy density
ED_m=120;%mean of energy density
ED_v=400;%variance of energy density
mu = ED_m;
sigma = sqrt( ED_v );
energy_density=zeros(N_simu,1);
num=1;
while(num<=N_simu)
   interm=randraw('norm',[mu,sigma]);
   if interm>0
      energy_density(num)=interm;
      num=num+1;
   end
end

%Calculate parameters of lognormal distribution_Cycle life
CL_m=3000;%mean of cycle life
CL_v=360000;%variance of cycle life
mu = log(CL_m) - 1/2*log(1 + CL_v/(CL_m)^2);
sigma = sqrt( log( 1 + CL_v/(CL_m)^2) );
cycle_life=randraw('lognorm',[mu,sigma],N_simu);
```

```
%Fixed values
DOD=0.8;
required_cycle=1000;%Based on ABC standard
alpha=0.054;%VSP energy coefficient
beta=133;%VSP energy coefficient
charging_loss=0.1;
W_singlecell=0.05;%Single cell weight
EI_singlecell=0.1099;%EI99 points of calcination LFP
EI_others=605.5;%EI99 points of EV excluding battery
EI_perkwh=0.0326;%EI99 points of 1 kwh electricity at US grid
EI_permile=0.0231;%EI99 points of 1 mile

%Environmental impact of ICEV
ICEV=615.5+EI_permile*120000;
EI_EV=zeros(N_simu,4);
count=0;

%Assume a totoal battery pack size of 40kwh based on ABC standard.
for i=1:N_simu
   clear Bat_mass N_cell
   Bat_mass=40/energy_density(i)*1000;
   N_cell=ceil(Bat_mass/W_singlecell);
   clear N-bat eff_last energy_efficiency range elec_con EI comp
      N_bat=ceil(required_cycle/cycle_life(i));
      %Final efficiency of the last functional battery pack
      eff_last=1-rem(required_cycle,cycle_life(i))*0.2/cycle_life(i);
      %Average energy efficiency of all battery packs
      energy_efficiency=1-(0.2*cycle_life(i)*fix(required_cycle/cycle_life(i))...
         +(1-eff_last)*rem(required_cycle,cycle_life(i)))/(2*required_cycle);
      %Range
      range=DOD*energy_density(i)*Bat_mass*energy_efficiency/(Bat_mass...
         *alpha+beta)*0.6213712;

      elec_con=40*(1+charging_loss)/range;

      %Calculate environmnetal burden of EV
      EI=EI_singlecell*N_cell*N_bat+EI_others+EI_perkwh*elec_con*120000;

      %Compare environmnetal imapcts of EI and ICEV
      if(EI<ICEV)
         count=count+1;
      end

      %Write output into EI_EV matrix
      EI_EV(i,1)=energy_density(i);
      EI_EV(i,2)=cycle_life(i);
      EI_EV(i,3)=EI;
      EI_EV(i,4)=(EI-ICEV)/ICEV*100;
end

n_elements=histc(EI_EV(:,4),(-80:0.5:80));
c_elements=cumsum(n_elements);
```

```
clf
figure(1)
low=min(energy_density);
high=max(energy_density);
hist(energy_density,(fix(low):0.5:ceil(high)));
title('Histogram of energy density');

figure(2)
mi=min(cycle_life);
ma=max(cycle_life);
hist(cycle_life,(fix(mi):2:ceil(ma)));
title('Histogram of cycle life');

figure(3)
bar((-80:0.5:80),n_elements/(N_simu));
axis tight
title('PDF of BEV outperforms ICEV');

figure(4)
bar((-80:0.5:80),c_elements/(N_simu));
axis tight
title('CDF of BEV outperforms ICEV');
```

3.4.7 Selected LCIA Results

Selected LCIA results that were not included in the manuscript were displayed in Figure S3-2, S3-3 and Table S3-13, S3-14.

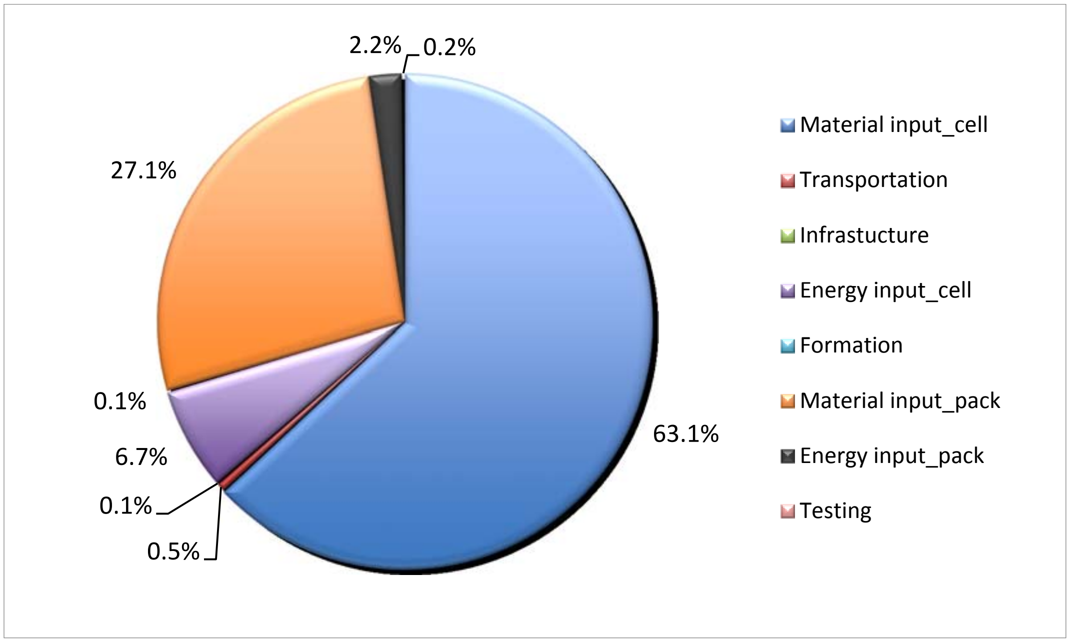

Figure S3-5. EI99 single core breakdown for manufacturing and assembly of LMO LIB pack

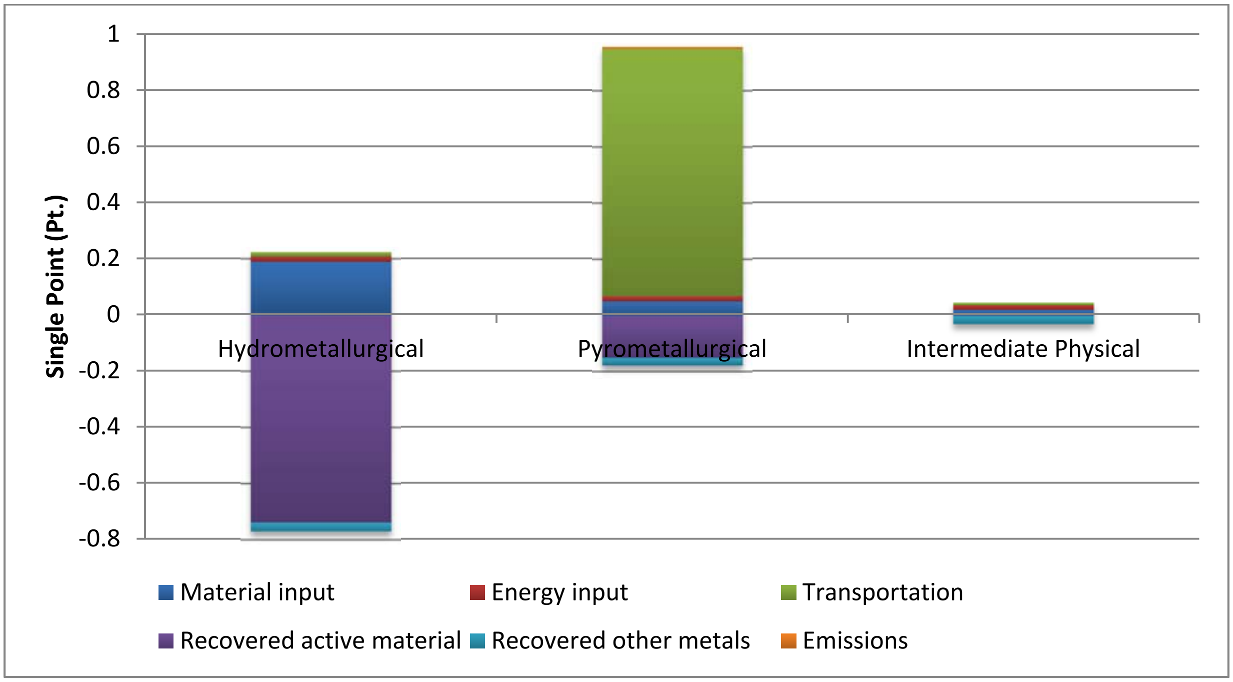

Figure S3-6. Spent LIB recycling processes comparison by EI99

Table S3-15. LCIA results of single NCM LIB cell evaluated by EI99

Impact category	Unit	Total	NCM	Graphite	LiPF6	Carbon black	EC	PVF	PET	PE	Steel	Cu	Al	Transport
Total	Pt	0.165769	0.080815	0.001682	0.001466	0.000235	0.00063	0.001456	0.000133	0.000187	0.00995	0.067586	0.001522	0.000107
Carcinogens	Pt	0.072767	0.024206	0.000213	0.000187	3.22E-06	5.28E-05	0.000133	9.14E-06	6.27E-07	0.000355	0.047343	0.000257	6.92E-06
Resp. organics	Pt	1.75E-05	9.42E-06	4.28E-06	2.02E-07	2.45E-08	1.17E-06	2.72E-07	4.69E-08	1.22E-07	5.38E-07	1.15E-06	1.97E-07	4.04E-08
Resp. inorganics	Pt	0.042032	0.031513	0.001054	0.00067	2.51E-05	6.18E-05	0.000362	1.51E-05	1.61E-05	0.002403	0.005407	0.000471	3.47E-05
Climate change	Pt	0.002352	0.001585	9.36E-05	9.17E-05	8.81E-06	3.26E-05	0.000149	6.87E-06	8.11E-06	0.000189	6.24E-05	0.000117	7.24E-06
Radiation	Pt	6.62E-05	4.81E-05	5.91E-07	3.87E-06	1.45E-08	6.82E-07	2.91E-06	1.49E-07	5.25E-10	4.63E-06	1.86E-06	3.08E-06	2.44E-07
Ozone layer	Pt	9.9E-07	6.32E-07	4.64E-08	1.22E-07	2.43E-08	5.12E-09	4.63E-08	1.58E-09	1.39E-11	4.97E-08	2.37E-08	3.5E-08	3.94E-09
Ecotoxicity	Pt	0.018339	0.005014	3.33E-05	5.28E-05	1.22E-06	1.42E-05	3.39E-05	5.1E-06	1.49E-07	0.003228	0.009901	5.19E-05	3.36E-06
Acidification/Eutrophication	Pt	0.002496	0.002048	3.61E-05	4.4E-05	1.31E-06	5.13E-06	3.45E-05	1.2E-06	1.53E-06	5.29E-05	0.000245	2.19E-05	3.94E-06
Land use	Pt	0.00108	0.000815	3.19E-05	2.44E-05	7.57E-07	3.33E-06	1.33E-05	7.39E-07	6.96E-09	4.78E-05	0.000126	1.36E-05	2.45E-06
Minerals	Pt	0.014299	0.00702	2E-06	2.76E-05	7.35E-07	9.14E-06	1.37E-05	1.56E-06	2.41E-09	0.002917	0.004177	0.000129	1.25E-06
Fossil fuels	Pt	0.01232	0.008556	0.000213	0.000365	0.000194	0.000449	0.000713	9.35E-05	0.00016	0.000751	0.000323	0.000456	4.66E-05

Table S3-16. Monte Carlo simulation results: percentages of BEV outperforming ICEV

		NCM	LMO	LFP
U.S.	EI99	60.29%	66.66%	99.63%
	CED	84.98%	90.86%	99.82%
	GWP	97.60%	99.02%	99.99%
U.S. (70%)	EI99	82.83%	99.23%	99.62%
	CED	91.00%	100.00%	99.84%
	GWP	98.49%	73.70%	99.99%
Brazil(FFV)	EI99	99.90%	100.00%	100.00%
	CED	100.00%	99.96%	100.00%
	GWP	99.99%	100.00%	100.00%
China	EI99	40.09%	44.61%	96.98%
	CED	99.96%	100.00%	100.00%
	GWP	69.47%	65.56%	99.01%
France	EI99	82.78%	98.53%	100.00%
	CED	58.88%	53.27%	97.90%
	GWP	100.00%	100.00%	100.00%
Germany	EI99	64.39%	85.32%	99.92%
	CED	78.48%	85.85%	99.73%
	GWP	99.43%	99.81%	100.00%
India	EI99	0.00%	0.00%	0.00%
	CED	0.00%	0.00%	0.00%
	GWP	0.00%	0.00%	0.00%
India (BS)	EI99	0.00%	0.00%	0.00%
	CED	28.28%	15.02%	85.05%
	GWP	0.00%	0.00%	0.00%

References

1. Lee, M.H.; Kang, Y.J.; Myung, S.T.; Sun, Y.k.. Synthsis optimization of Li[$Ni_{1/3}Co_{1/3}Mn_{1/3}$]O_2 via co-precipitation. *Electrochimica Acta*. 2004, 50, 939-948.

2. Todorov, Y.M.; Numata, K.. Effects of the Li: (Mn+Co+Ni) molar ratio on the electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material. *Electrochimica Acta*. 2004, 50, 495-499.

3. Nukuda, T.; Inamasu, T.; Fujii, A.; Endo, D.; Nakagawa, H.; Kozono, S.; Iguchi, T.; Kuratomi, J.; Kohno, K.; Izuchi, S.; Oshitani, M.. Development of a lithium ion battery using a new cathode material. *J. Power Sources*.2005, 146, 611-616.

4. Yamada, A.; Chung, S.C.; Hinokuma, K. Optimized $LiFePO_4$ for lithium battery cathodes. *J. Electrochem. Soc.* 2001, 148, A224-A229.

5. Garcia-Moreno, O.; Alvarez-Vega, M.; Garcia-Alvarado, E.; Garcia-Jaca, J.; Gallardo-Amores, J.M.; Sanjuan, M.L.; Amador, U.. Influence of the structure on the electrochemical performance of lithium transition metal phosphates as cathodic materials in rechargeable lithium batteries: a new high-pressure form of $LiMPO_4$ (M=Fe and Ni). *Chem. Mater.* 2001, 13, 1570-1576.

6. Majeau-Bettez, G.; Hawkins, T.R.; Stromman, A.H. Lief cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. *Environ. Sci. Technol.* 2011, 45, 4548-4554.

7. Notter, D. A.; Gauch, M.; Widmer, R.; Wager, P.; Stamp, A.; Zah, R.; Althaus, H.-J. Contribution of Li-ion batteries to the environmental impact of electric vehicles. *Environ. Sci. Technol*. 2010, 44, 6550–6.

8. Dunn, J.B.; Gaines, L.; Barnes, M.; Sullivan, J.; Wang, M. *Material and energy flows in the materials production, assembly, and end-of-life stages of the automotive Lithium-ion battery life cycle*. Center for Transportation Research, Energy System Division, Argonne National Laboratory, Illinois, U.S., 2012.

9. *Advanced dry room concepts*, Harris Environmental Systems; http://www.harris-env.com/korea_paper.htm

10. *Dry room paper*, Harris Environmental Systems; http://www.harrisenv.com/images/Dry%20Room%20Paper,%202001%20Florida%20Battery%20Seminar.ppt

11. Jang, M.W.; Jung, H.G.; Scrosati, B.; Sun, Y.K.. Improved co-substituted, $LiNi_{0.5-x}Co_{2x}Mn_{1.5-x}O_4$ lithium ion battery cathode materials. *J. Power Sources*.2012, 220, 354-359.

12. Omar, N.; Verbrugge, B.; Mulder, G.; Van den Bossche, P.; Van Mierlo, Joeri; Daowd, M.; Dhaens, M.; Pauwels, S.. Evaluation of performance characteristics of various lithium-ion batteries for use in BEV application. *Vehicle Power and Propulsion Conference (VPPC),* September 1-6, 2010.

13. Hohne, K.; Hirtz, E.. With system integratin and lightweight design to highest energy densities. *Advanced Microsystems for Automotive Application 2013*. Lecture Notes in Mobility 2013, 205-214.

14. Yi, T.F.; Hao, C.L.; Yue, C.B.; Zhu, R.S.; Shu, J. A literature review and test: structure and physicochemical properties of spinel $LiMn_2O_4$ synthesized by different temperatures for lithium ion battery. *Synthetic Met.* 2009, 159, 1255-1260.

15. Liu, W.; Farrington, G.C.; Chaput, F.; Dunn, B. Synthesis and electrochemical studies of spinel phase $LiMn_2O_4$ cathode materials prepared by the Pechini process. *J. Electrochem. Soc.* 1996, 143, 879-884.

16. Park, Y.J.; Lim, J.G.; Kim, M.K.; Chung, H.T.; Kim, H.G. Preparation of $LiMn_2O_4$ thin films by a sol-gel method. *Solid State Ionics*. 2000, 130, 203-214.

17. Subramania, A.; Angayarkanni, N.; Vasudevan, T. Effect of PVA with various combustion fuels in sol-gel thermolysis process for the synthesis of $LiMn_2O_4$ nanoparticles for Li-ion batteries.

Mater. Chem. Phys. 2007, 102, 19-23.
18. Sun, Y.K.; Oh, I.H.; Kim, K.Y. Synthesis of spinel $LiMn_2O_4$ by the sol-gel method for a cathode-active material in lithium secondary batteries. *Ind. Eng. Chem. Res.* 1997, 36, 4839-4846.
19. Li, T.; Qiu, W.H.; Zhao, R.H.; Xia H.; Zhao, H.L.; Liu, J.J. Effects of sintering time on the electrochemical properties of spinel $LiMn_2O_4$ synthesized by solid-state reaction. *J. Univ. Sci. Technol. B.* 2008, 15, 74-78.
20. *Kokam Superior Lithium Polymer Battery (SLPB) Cell Specification Data*. Kokam Co. Ltd: Korea, 2009;
http://www.elektronik.ropla.eu/pdf/stock/kok/tech_spec_slpb120216216_53ah.pdf
21. *Lithium Ion Battery*. LG Chem Power Inc.;
http://www.lgcpi.com/lithium.shtml
22. *AMP 20 Prismatic Pouch Cell Data Sheet.* A123 System, Inc.;
http://www.a123systems.com/prismatic-cell-amp20.htm
23. Takahashi, M.; Ohtsuka, H.; Akuto, K.; Sakurai, Y. Confirmation of long-term cyclability and high thermal stability of $LiFePO_4$ in prismatic lithium-ion cells. *J. Electrochem. Soc.* 2005, 152, A899-A904.
24. Choi, D. and Kumta, P.N. Surfactant based sol-gel approach to nanostructured $LiFePO_4$ for high rate Li-ion batteries. *J. Power Sources.* 2007, 163, 1064-1069.
25. Prosini, P.P.; Cianchi, L.; Spina, G.; Lisi, M.; Scaccia, S.; Carewska, M.; Minarini, C.; Pasquali, M. Synthesis and characterization of amorphous $3Fe_2O_3.2P_2O_5.10H_2O$ and its electrode performance in lithium batteries. *J. Electrochem. Soc.* 2001, 148, A1125-A1129.
26. Xu, Z.H.; Xu, L.; Lai, Q.Y.; Ji, X.Y. A PEG assisted sol-gel synthesis of $LiFePO_4$ as cathodic material for lithium ion cells. *Mater. Res. Bull.* 2007, 42, 883-891.
27. Doeff, M.M.; Hu, Y.Q.; McLarnon, F.; Kostecki, R. Effect of surface carbon structure on the electrochemical performance of $LiFePO_4$. *Electrochem. Solid St.* 2003, 6, A-207-A209.
28. *Electricity/heat in India in 2009*, International Energy Agency;
http://www.iea.org/stats/electricitydata.asp?COUNTRY_CODE=IN
29. *Coal in the Energy Supply of India;* Coal Industry Advisory Board/International Energy Agency: Paris, France, 2002.
30. *Anthropogenic Emissions from Energy Activities in India*: Generation and Source Characterization, Program for Computational Reactive Mechanics (PCRM). Ohio Supercomputer Center;
http://www.osc.edu/research/archive/pcrm/emissions/thermalemissions.shtml
31. Chakraborty, N.; Mukherjee, I.; Santra, A.K.; Chowdhury, S.; Chakraborty, S.; Bhattacharya, S.; Mitra, A.P.; Sharma, C. Measurement of CO_2, CO, SO_2 and NO emissions from coal-based thermal power plants in India. *Atmos. Environ.* 2008, 42, 1073-1082.
32. *World Energy Outlook 2007: China and India Insight;* International Energy Agency: Paris, France, 2007.
33. *Country Analysis Briefs: India*. EIA;
http://www.eia.gov/countries/cab.cfm?fips=IN
34. *Country Analysis Briefs: China*. EIA;
http://www.eia.gov/countries/cab.cfm?fips=CH
35. *Country Analysis Briefs: Brazil*. EIA;
http://www.eia.gov/countries/cab.cfm?fips=BR
36. *Average Fuel Efficiency of U.S. Light Duty Vehicles*. Research and Innovative Technology Administration, Bureau of Transportation Statistics;
http://www.bts.gov/publications/national_transportation_statistics/html/table_04_23.html
37. *Light-Duty Vehicle, Light-Duty Truck, and Medium-Duty Passenger Vehicle – Tier 2 Exhaust Emission Standards.* US EPA;
http://www.epa.gov/oms/standards/light-duty/tier2stds.htm
38. Schmitt, W.F.; Szklo, A.; Schaeffer, R. Policies for improving the efficiency of the Brazilian

light-duty vehicle fleet and their implications for fuel use, greenhouse gas emissions and land use. *Energ. Policy*. 2011, 39, 2163-3176.
39. Wills, W.; La Rovere, E.L. Light vehicle energy efficiency programs and their impact on Brazilian CO_2 emissions. *Energ. Policy*. 2010, 38, 6453-6462.
40. *Brazilian Automotive Industry Yearbook 2011*; Brazilian Automotive Industry Association: Sao Paulo, Brazil, 2011.
41. Salvo, A.; Huse, C. Build it, but will they come? Evidence from consumer choice between gasoline and sugarcane ethanol. http://www.kellogg.northwestern.edu/faculty/salvo/htm/fuelchoice.pdf
42. Huo, H.; Yao, Z.L.; He, K.B.; Yu, X. Fuel Consumption rates of passenger cars in China: Labels versus real-world. *Energ. Policy*. 2011, 39, 7130-7135.
43. Wang, H.K.; Fu, L.X.; Bi, J. CO_2 and pollutant emissions from passenger cars in China. *Energ. Policy*. 2011, 39, 3005-3011.
44. *Emission Norms.* Society of Indian Automobile Manufacturers; http://www.siamindia.com/scripts/emission-standards.aspx
45. Chugh, R.; Cropper, M.; Narain, U. The cost of fuel economy in the Indian passenger vehicle market. *Energ. Policy*. 2011, 39, 7174-7183.

Chapter 4

Life Cycle Comparison of Personal Transportation Options Powered by Natural Gas

4.1 Introduction

Natural gas has long been considered a cleaner fuel than coal or petroleum, yet its higher cost has hindered its deeper penetration into energy markets. The application of horizontal drilling and hydraulic fracturing technologies in recent years has made the economic production of shale gas possible. According to the U.S. Energy Information Administration (EIA), U.S. shale gas production maintained an annual growth of 48% from 2006 to 2010.[1] Moreover, a 113% increase in the total production of shale gas from 2010 to 2040 is predicted in the *2013 Annual Energy Outlook*.[2] Because of the lower cost and lower carbon footprint of natural gas, the EIA predicts an annual growth rate of 11.9% for direct consumption of natural gas in the transportation sector from 2011 to 2040.[2] Also, natural gas is expected to fire 63% of the thermoelectric power plants added in the United States between 2012 and 2040.[2] A portion of this electricity could serve as the power source for electric vehicles. Since the direct or indirect use of natural gas for personal mobility is almost certain to increase in the coming decades, the environmental impacts associated with the delivery of passenger vehicle miles are worthwhile to investigate for alternative modes of natural gas utilization in the transportation sector.

With current technology, natural gas-powered passenger vehicles that are presently in operation, or will soon be available, either directly burn compressed natural gas or possess proton exchange membrane fuel cells (PEMFC) that use chemical derivatives of natural gas for their fuel. BEVs have also been advanced as an alternative to PICVs to reduce energy consumption and CO_2 emissions in the transportation sector. Since the fraction of electricity produced from natural gas combustion turbines or combined cycle power plants will steadily rise in the foreseeable future, BEVs powered using this electricity similarly constitute an important component of natural gas-based mobility.

Among the aforementioned transportation options, BEVs have received the most attention from life cycle practitioners and researchers.[3-6] As a major constituent of the light-duty passenger fleet in a few countries where natural gas production is self-sufficient, CNGVs have also been the focus of a handful of environmental studies.[7-12] Knowledge gaps, however, exist for FCVs. Although a few life cycle analyses have been conducted on PEMFCs for stationary power plant or automobile applications,[13-16] a detailed life cycle inventory (LCI) for the PEMFC stack has not been reported, most likely for proprietary reasons since FCVs are still in their demonstration phase. The absence of an LCI makes it difficult to validate the conclusions from previous studies against uncertainties with regard to material and energy flows in the FCV life cycle.

Additionally, to date no complete LCA study has been done to compare the life cycle impacts of delivering mobility using natural gas as the same fuel source directly or indirectly for different personal passenger vehicles. The GREET model[17] does offer life cycle GHG emission, total energy consumption and criteria air pollutants emissions for light-duty vehicles, but it does not model the vehicle cycle of the FCV and the operation of BEV in depth, nor does it provide emission other than the criteria air pollutants, such as copper, arsenic and lead, which can be consequential when modeling the impacts of human health and ecosystem quality. Therefore, the output of the GREET model does not provide sufficient information on which natural gas powered mobility options offer the utmost environmental benefits and what improvements can be made to reduce the environmental impacts associated with driven miles. To bridge this knowledge gap, in this study, the environmental impacts of delivering driven vehicle miles are compared for three different vehicle fleets, each powered either directly or indirectly by natural gas. The fleets studied are BEVs, using electricity generated from natural gas combined cycle (NGCC) power plants; CNGVs, which are internal combustion engine vehicles modified to burn compressed natural gas; and FCVs powered by hydrogen produced from steam methane reforming (SMR) of natural gas. The overarching goal of the LCA study is to assess which mode of natural gas-based personal passenger mobility offers the most compelling future environmental benefits, as both the civil power infrastructure and the transportation sector undergo a greening transition from coal and petroleum respectively to natural gas.

4.2 Methodology

A process based LCA was conducted for BEV, CNGV, and FCV personal mobility using natural gas as the exclusive primary fuel source. The system boundary is depicted in Figure 1. The functional unit was defined to be 120,000 miles evenly delivered over a 10-

year period. A mid-sized petroleum passenger PICV driven in the U.S.[18-19] was also investigated as a basis for comparison.

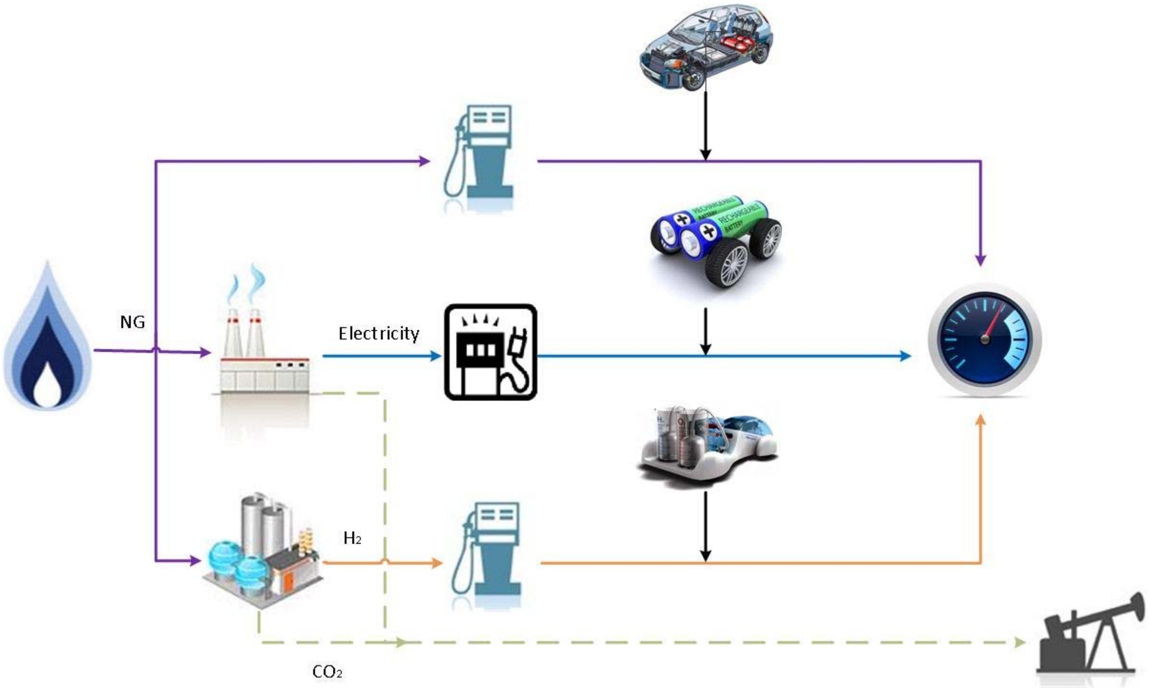

Figure 4-1. System Boundary

The three fleets studied were assumed to have the same glider and similar power train configuration, excluding power source parts. In all three cases, power generation methods were chosen based on best-in-class or near best-in-class components that are nonetheless widely commercially available (commoditized). Table 4-1 shows several commercially available systems for each category, manufacturers of these systems, and estimates for the costs of the components purchased at scale.[20-28]

For the BEV, the energy source is a lithium-ion battery (LIB) using $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM)[29] for its cathode active material. NCM was chosen for its demonstrated specific energy of 135 kWh/kg and cycle life of 1300.[30] The details of modeling the assembly of the LIB and the drive cycle of the BEV are given in the supporting information (SI).

For the CNGV, the energy source is an internal combustion engine (ICE) using a four-stroke Otto cycle,[31] which is the same spark ignition engine cycle used in PICVs. It is assumed that the CNGV is fueled by natural gas contained within a 100 kg chrome steel storage tank.[32] The energy source for the FCV was chosen to be an 80 kW PEMFC and a 20 kW LIB,[33] also based on the NCM cathode chemistry. The LCI of the PEMFC is based on a cost analysis[34], in which PEMFC composition and descriptions on the synthesis of its major components are provided.

Table 4-1. Commercially available passenger vehicles for the three mobility alternatives.

	Make	Model	MSRP
CNGV	Honda	Civic GX	$26,305
BEV	Nissan	Leaf S	$28,800
	Mitsubishi	i-MiEV	$22,995
	Chevrolet	Spark EV	$27,495
	Ford	Focus Electric	$35,200
FCV	Honda	FCX Clarity	lease $600/month for 3 years
	Hyundai	Tucson Fuel Cell	lease $499/month for 3 years
	Mercedes-Benz	B-Class F-Cell	lease $849/month for 2 years

The infrastructures for the three systems studied reflect present civil and business norms in 2010. In each case, materials and energy consumption for fuel generation and processing were included in the accounting of costs, starting from an assumed common energy source of sale-quality processed natural gas. The BEV natural gas utilization pathway consists of a NGCC thermoelectric power plant and BEV charging stations[37]. The CNGV route is comprised of natural gas fuel stations with onsite compression supplied from electricity-powered pumps.[6] The infrastructure for FCVs consists of SMR plants[38] and hydrogen fueling stations with onsite compression[39].

The materials and energy used for the construction of the fuel conversion facilities (SMR plants for FCVs; NGCC plants for BEVs), fuel delivery infrastructure (tanker trucks for FCVs; natural gas distribution pipelines for CNGVs; transmission lines for BEVs) and vehicle fueling stations (pumps for CNGVs and FCVs; charging devices for BEVs) were not included in the LCIs, because these infrastructure contributions to the life cycle environmental impact are insignificant (<1%) in comparison to the operational impacts, based on previous U.S. Department of Energy LCA studies on energy systems[35-36] Charging losses for BEVs, and energy consumption for the compression of natural gas and hydrogen for their respective use in CNGVs and FCVs, are significant and are therefore fully accounted for in the LCI. The fuel economy and emissions of CNGVs were obtained from the EPA vehicle emission database[40-41], while information for FCVs was collected from the report on national FCV demonstration[39]. Complete LCIs of the vehicle energy sources and their supporting infrastructures are reported in the SI.

Data produced by individual LCIs are often highly variable, given that studies commonly stem from laboratory to commercialization phase scales. To test the robustness of our study to different choices in the LCI data sources, a sensitivity analyses is incorporated.

Values of key technology parameters are collected from published studies, ranging from commercialized applications to laboratory test data.[2, 5, 7, 12, 30, 32, 34, 37-53]. Averages and standard deviations were determined for each parameter as shown in Table 4-2. Normal distribution was assumed for all the parameters except for NCM battery properties, for which lognormal distribution was assumed. For parameters for which the assumed distribution could sample values that are beyond the acceptable range, upper bounds and lower bounds were determined based on maximum and minimum values for these parameters found in literature, so that sampled values above the upper bound or below the lower bound would be rejected in the Monte Carlo Simulation. All of the parameters listed in Table 4-2 were obtained from reports at the demonstration or commercialization scale, save for the NCM battery properties which were obtained from pilot and laboratory scale studies. Monte Carlo simulations with 10,000 realizations were carried out for each transportation mode. Asymptotic analysis is summarized in Table S4-18 of the SI.

Table 4-2. Statistical Summary for Key Technology Parameters

	NCM cycle life	NCM specific energy	NGCC efficiency	NGCC efficiency w/CCS	FC Pt loading	SMR efficiency	SMR efficiency w/CCS	FCV FE*	CNGV tank mass	CNGV FE*
Unit	#	Wh/kg	%	%	mg/cm^2	%	%	MPG	kg	MPG
Mean	1300	135	50.2	42.8	0.3	82.5	77.8	50	100	31
SD	±300	±20	±5	±10	±0.3	±5	±10	±5	±20	±5
Upper	N/A	N/A	61	53.5	0.75	89.3	84.6	60	N/A	36
Lower	N/A	N/A	41.7	32.7	0.1	69.1	50.8	36	N/A	21.6

*fuel economy in miles per gallon

Since BEV and FCV give off no tailpipe emissions, and the centralized well-to-fuel conversion process makes CCS a possibility for these mobility options, CCS scenarios were constructed for a NGCC power plant and a SMR plant. Both CCS processes use monoethanolamine (MEA) as the absorbent, and the LCI for the carbon capture processes for the respective fuel conversion plants were adapted from two U.S. DOE national laboratory reports in which detailed technology descriptions were provided for systems with and without CCS[37, 38] . For the sequestration process, LCI information is unavailable due to the limited large-scale practice of carbon sequestration. In this analysis, geological storage of captured CO_2 in saline formations was assumed, as these formations collectively represent the vast majority of the identified storage volume for geologic CO_2 sequestration.[54] The infrastructure is represented by a 300 km pipeline, an estimate based on the average distance between large point sources of CO_2 and areas with formations suitable for geological sequestration.[54] Energy consumption for pipeline transport, recompression of CO_2 at the well, and injection into the formation was approximated with comparable values estimated for geological CO_2 sequestration with oil recovery.[55]

Material and energy inputs were obtained from Ecoinvent database 2.2.[56] The environmental impacts were evaluated by ReCiPe midpoint method with the hierarchic perspective;[57] Cumulative Energy Demand (CED) v 1.07, and IPCC 2007 100-year global warming potential (GWP) respectively. Life cycle impact assessment was done using SimaPro 7.2. Detailed information of the life cycle inventories is available in Tables S1 through S21 of the Supporting Information.

4.3 Results and Discussion

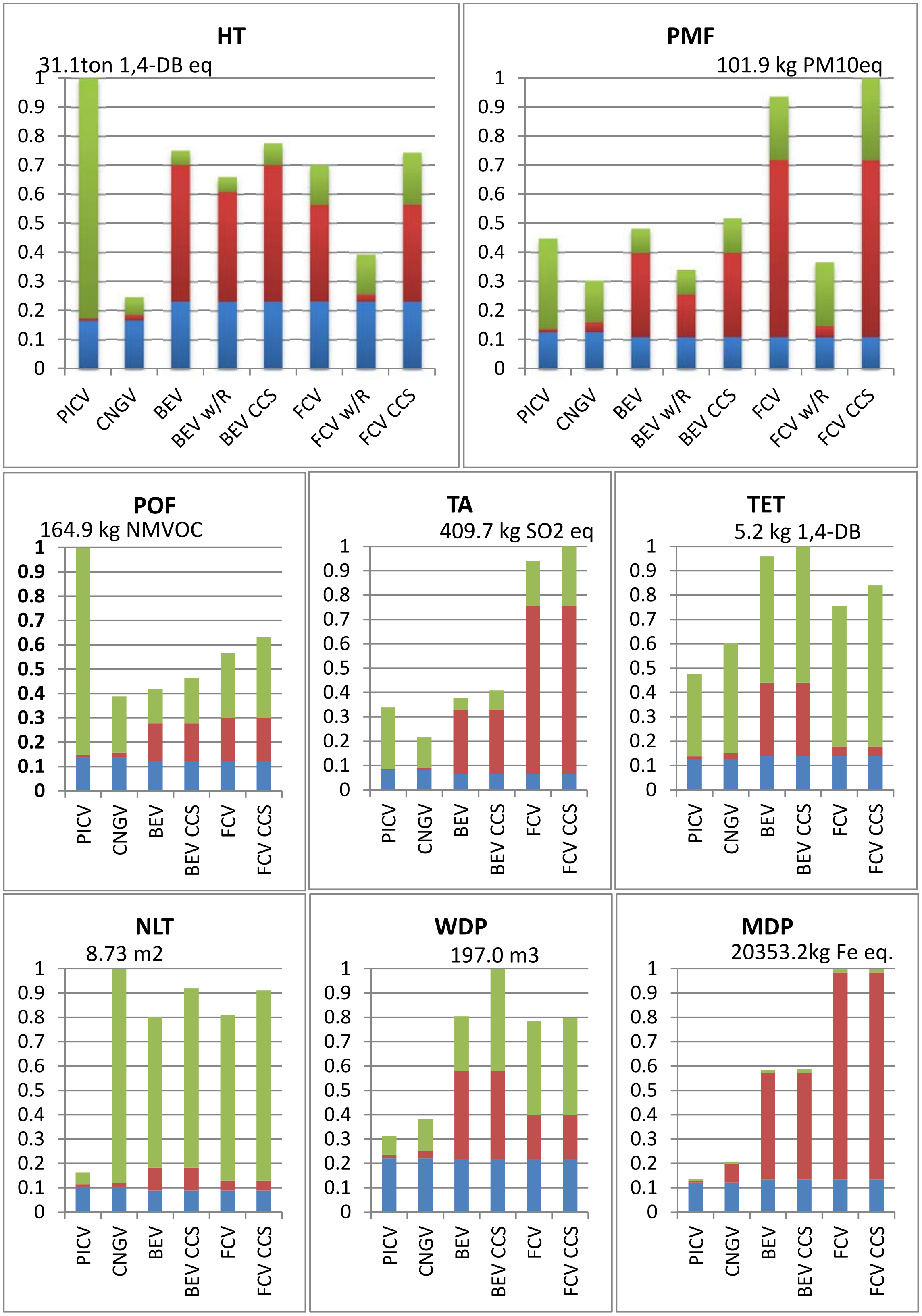

Figure 4-2. Comparison of the ReCiPe midpoint indicators for the three mobility options fueled using natural gas, normalized to the vehicle with the highest impact

for each indicators. The blue bars represent the glider and the drivetrain; the red bars represent the power source; the red bars represent the use phase.

Figure 4-2 summarized the life cycle environmental impacts of the three natural gas-based mobility options as opposed to IPCV evaluated by 9 selected ReCiPe midpoint indicators: human toxicity (HT), photochemical oxide formation (POF), particulate matter formation (PMF), terrestrial acidification (TA), terrestrial toxicity (TET), natural land transformation (NLT), water depletion (WDP), metal depletion (MDP) and fossil depletion (FDP). The 9 indicators were chosen based on their relatively significant potential for human health damage, ecosystem quality deterioration and resources depletion. Among the 18 ReCiPe midpoint indicator scores for the natural gas-powered vehicles, climate change has the most substantial impact on human health and ecosystem, but it's not reported here due to overlapping with GWP.

As can be observed from Figure 4-2, PICV results in the highest environmental burden in the impact categories of HT, POF and FDP, which are all largely driven by the use phase of PICV. The HT score can be traced back to barium emission into water during the crude oil production. The POF score is the combined result of NO_x, none-methane volatile organic compounds and CO emissions, both from petroleum refining and PICV operation. The FDP score is primarily due to crude oil consumption. CNGV tops the indicators of NLT. The NLT impact is caused by additional high pressure natural gas pipeline demand. FCV has the highest environmental impacts with regard to PMF, TA and MDP, which mostly stem from platinum content in the PEMFC. SO_2 emission from platinum refining, in particular, is responsible for the elevated PMF and TA score pertaining to the power source of FCV. BEV becomes the least favorable mobility option when the comparison is based on TET and WDP. In addition to copper emissions from tire abrasions, which exist for all the four types of vehicles, the use phase TET score for BEV can be attributed to phosphorus emissions from natural gas extraction, mercury emissions from power plant and copper emissions from electricity transmission. The WDP score for the LIB is due to sulfuric acid and direct water consumption for the refining of cobalt and nickel, while evaporative cooling water loss accounts for the use phase score.

HT and PMF, along with CED and GWP, were then chosen as the metrics for uncertainty analysis. The results were presented in Figure 4-3.As shown by the four life cycle environmental impact indicator scores of Figure 4-3, the HT, CED and GWP impacts for all three categories of natural gas-powered vehicles are lower than those for the PICV, unless very conservative estimates are made for the technology parameters of the natural gas-powered transportation options (as reflected in the upper bounds on the confidence intervals). The results evaluated by CED and GWP indicate that the use phase is the single largest contributor to the overall environmental footprint across different vehicle configurations, which represents 52% to 86% of the total life cycle impact. When comparing across the three natural gas mobility options, the BEV has the smallest use phase environmental footprint, followed by FCV and CNGV. These findings are in good agreement with the output of the GREET model. Also, it is consistent with the ranking of the overall well-to-wheel energy conversion efficiencies of the three vehicles. The BEV, with an extremely efficient (~90%) electric power train and a moderately efficient

(~50%) natural gas-to-electricity conversion infrastructure, has a well-to-wheel efficiency of around 40%. The efficiency of a PEMFC meanwhile is slightly above 40%. When coupled with an 80% efficient SMR plant, this yields an overall energy conversion efficiency about 30% for a FCV. Trailing in efficiency is the CNGV, particularly CNGVs that are retrofitted from gasoline engines. For CNGVs, the fuel conversion efficiency is approximately 20%.[8]

As can be seen in Figure 4-3, the assembly-phase impacts for the power sources of the BEV and FCV (i.e. the LIB and the PEMFC, respectively) both contribute significantly to the environmental footprint for mobility using these vehicles. This is notably so for the the environmental impact categories of HT and PMF. For BEVs, the LIB accounts for 63% of the life cycle HT score, 63% of PMF, 11% of CED, and 11% of GWP. The cathode active material, NCM, within the LIB is the largest single contributor to the LIB HT and PMF score. The large environmental impact of NCM can be attributed to air emissions of sulfur dioxide, arsenic and lead, and water emissions of manganese, arsenic and selenium that are incurred in the mining and refining of nickel and cobalt. These emissions cause damage to human health from exposure to carcinogens and respiratory inorganics, and also impair ecosystem quality. Copper use in the anode current collector of the LIB is the second largest contributor to the LIB HT and PMF score, while the casings of the LIB cell and pack contribute significantly to the CED and GWP. Energy consumption incurred during the manufacturing and assembly phase, although not a dominant contribution, constitutes nearly 4.5% of the environmental burden associated with the LIB pack.

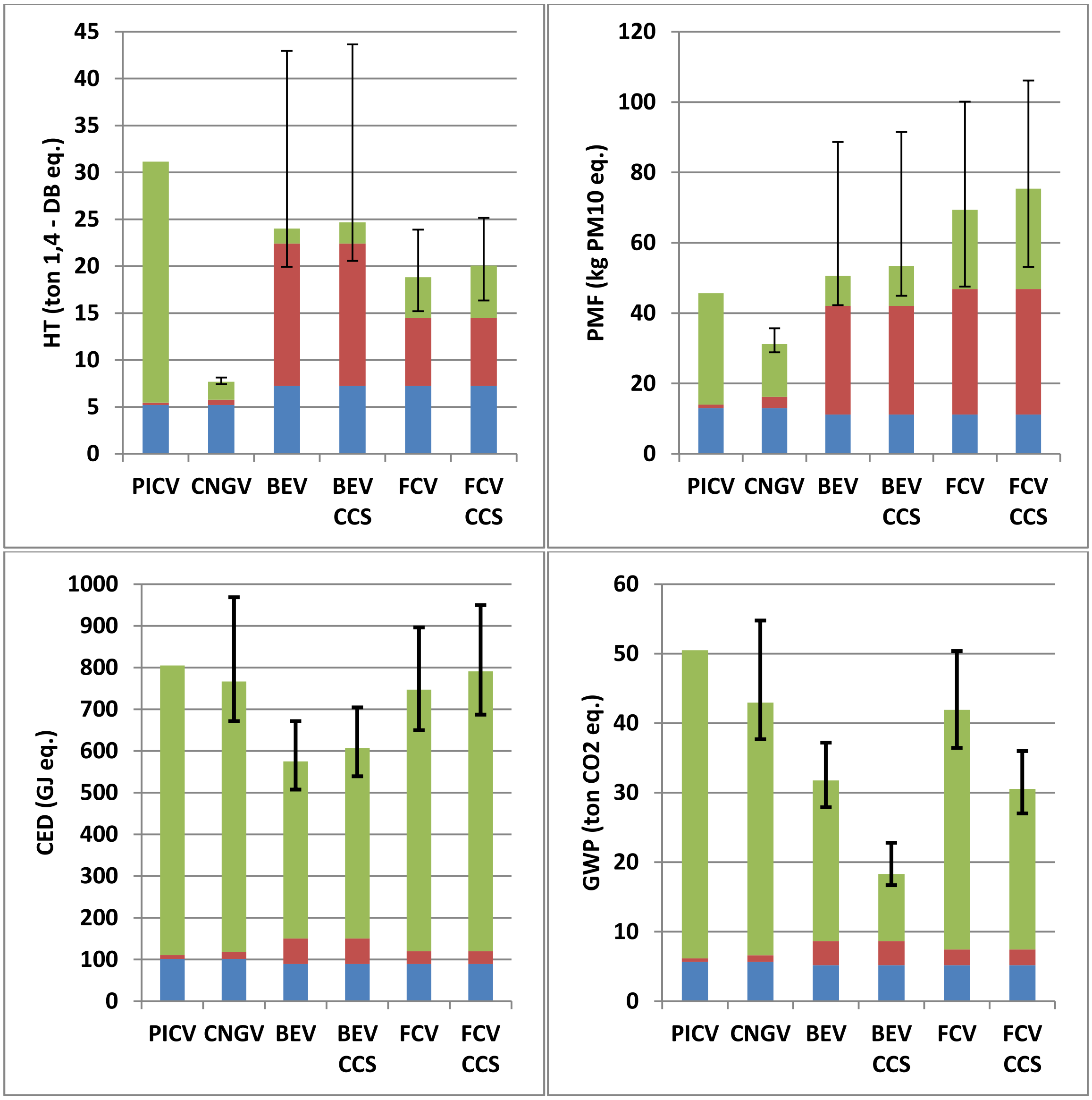

Figure 4-3. Comparison of HT, PMF, CED and GWP for the three mobility options fueled using natural gas. The colored bars show the averages of the Monte Carlo simulations. The error bars represent the 95% confidence interval.

For the FCV, the PEMFC makes up 39% of the HT score, 53% of the PMF, 4% of CED, and 5% of GWP. The principal environmental hot spot for PEMFCs is the platinum used as the catalyst at the electrodes. The refining process for platinum is similar to that for cobalt and nickel, and thus incurs comparable environmental impacts. In addition, as an extremely rare metal, platinum refining is more energy intensive. This translates into higher CED and GWP. The allocation method used for the platinum group metals (PGM) further drives up the emissions from platinum production, especially emissions of SO_2 and NO_x. In the Ecoinvent database, the extraction and refining of the PGM is modeled as a multi-output process, for which the refining burden is allocated exclusively to PGM, while the environmental burden from all other steps are allocated to all the process outputs, including nickel, copper and the PGM. When allocating the burden to each of the co-products, the allocation is based on revenue made, which results in a burden for the PGM that is more than 1,000 times greater than that of the other co-products, while the content of PGM in the ore is around 1% of that of the other co-products. Moreover, the waste generated from metallurgy and separation is recovered for construction materials. The revenue based allocation again attributes almost all of the environmental burden from this process to the PGM due to large price differences between the PGM and the construction materials. As a result, the platinum LCI obtained from the Ecoinvent database contains elevated emissions entries and subsequently leads to elevated environmental scores for platinum. For the reference case in which platinum loading at the electrodes is 0.75 mg/cm^2, platinum contributes 98% of the HT, 99% of PMF, 78% of CED, and 58% of GWP for assembly of the PEMFC. Other PEMFC components of note are the graphite bipolar plate, membrane and balance of plant, whose environmental impacts range from 3.7% to 20% when evaluated by GWP.

On account of the predominant contributions of platinum and NCM to the respective manufacturing phase environmental impacts of the PEMFC and LIB, the system boundaries were expanded to consider the effect of PEMFC and LIB recycling. Based on commercially available recycling technologies,[58,59] the environmental impact of the PEMFC can be reduced by 92% for HT, 94% for PMF, 65% for CED, and 48% for GWP by recycling its platinum content and reusing it to reduce primary platinum consumption. Current recycling technologies recover lithium, cobalt, and scrap metal from spent LIBs. The recovered lithium and cobalt content can then be used as starting materials for the synthesis of active cathode materials, so LIB manufacturing phase impacts can be reduced by 20% for the HT score, 50% for PMF, 41% for CED, and 26% for GWP by recovering these materials. It should be noted that however, in this study, no downcycling is assumed for both the platinum and the lithium and cobalt compounds. That is, the recycled materials are assumed to exhibit the same properties as the virgin materials. If downcycling were to be considered, the benefits from recycling might have been overestimated. On the other hand, the recycling technologies are expected to get more efficient due to economic incentives, which can further extend the merits of the recycling process. Therefore, the results obtained from this study can be considered an optimistic yet realistic representation of the actual benefits of recycling.

The results of the sensitivity analysis shown in Figure 4-3 indicate that despite uncertainties in key LIB performance parameters, it is highly probable that BEVs powered on natural gas electricity will have lower life cycle CED and GWP impacts compared with CNGVs for the same number of driven miles. Clearly, improving the vehicle fuel economy and/or the fuel infrastructure conversion efficiency will render any of the three vehicle options more environmentally benign. For the BEV, increasing the energy density of the cathode active material results in more lightweight LIB pack, which in turn reduces both the manufacturing phase and the use phase environmental footprints. The HT and PMF score of the BEV is particularly sensitive to the cycle life of NCM LIB, as a longer cycle life eliminates the need to replace the battery pack during the BEV lifetime, and thus avoids the significant add-on environmental burden of a replacement LIB pack.

To evaluate the effect of the LIB cathode chemistry on the life cycle environmental impacts for natural gas-based mobility, in Figure S4-1 a comparison is shown for a BEV powered by a NCM battery pack and BEV featuring a LIB with lithium manganese oxide (LMO) as the cathode active material. LMO battery packs are presently in service in demonstration and commercialization stage BEVs, but have a lower specific energy and cycle life than that projected for NCM pack chemistries currently in the pilot stages of development. On the other hand, LMO does not contain nickel and cobalt which can contribute to significant environmental issues as discussed earlier. Consequently, substitution of NCM for the LMO battery chemistry produces lower environmental impacts for BEV mobility for 9 of the 11 indicators shown in Figure S1, except for the environmental impact categories of FDP and MDP, and the HT, POF, FDP, CED and GWP remain much lower than for PICV mobility.

For FCV mobility, the required platinum loading at the PEMFC electrodes largely determines the life cycle environmental impact, as previously noted. It bears note that PEMFCs and LIBs, in contrast to internal combustion engines, are not well-established technologies and thus have more ample room for improvement. Considering that some of the performance parameters used in this study are based on data for LIBs and PEMFCs in their early stages of development, it is likely that future technological advancements will more significantly reduce the environmental impacts of next-generation BEVs and FCVs relative to CNGVs.

Another potential long-term advantage of BEVs or FCVs over CNGVs is that the conversion of natural gas into either electricity or hydrogen corrals the production of carbon dioxide from natural gas utilization into a smaller number of power plants or reforming facilities, rather than a large number of CNGV exhaust ports. This renders the deployment of CCS technology at NGCC power plants or SMR plants a practical option for BEVs or FCVs for greenhouse gas mitigation. As shown in Figure 4-3, a 43% reduction of life cycle GHG emissions for BEV mobility is achieved using CCS in tandem with NGCC electricity generation. A comparable 27% decrease is realized for FCV mobility when CCS is coupled with SMRP hydrogen production. As indicated in Figures 4-3, the greenhouse gas emission reductions obtained using CCS are won at the cost of a higher CED, HT and PMF footprint for BEVs and FCVs relative to CNGVs. For BEV natural gas mobility, the inclusion of CCS in the power generation infrastructure increases the HT score by 3%, the PMF by 5% and the CED by 6%. For FCV mobility, the environmental and energy footprints are amplified by 7%, 9%and 6% respectively. These increases can be attributed to the substantial parasitic energy penalty that is incurred when adding carbon capture and storage to power stations or fuel reforming facilities. As shown in Figures S4-2, the best available present-day CCS technology using MEA separation requires considerable input energy to recover the captured CO_2 from the solvent and to compress the concentrated CO_2 for pipeline transport to the sequestration site. Material and energy consumption for CO_2 capture at the NGCC power plant accounts for 71% of the CED, 22% of the PMF and 15% of the HT impact score for the entire CCS process, whereas energy used to transport the captured CO_2 by pipeline from the plant to the injection well accounts for most of the remaining impact (26%, 68% and 75% respectively for CED, PMF and HT). For CCS at a steam methane reforming plant, the respective contributions to the CED, PMF and HT score for the overall process are 61%, 57% and 48% for the capture stage and 36%, 38% and 46% for the pipeline transport phase. It should be noted that CO_2 absorption by MEA is one of the more mature yet energy intensive technologies for CCS, because MEA is generally recirculated in the adsorption unit as an aqueous solution. The high heat capacity of water notably raises the energy requirement for heat regeneration of the absorbent. The development of alternative CCS technologies, based on adsorption or membrane separation, might consume less energy and could thereby reduce the non-GHG environmental footprint associated with CCS.

References

[1]. *Annual Energy Outlook 2011 Reference Case.* U.S. Department of Energy, U.S. Energy Information Administration, Office of Integrated and International Energy Analysis, Washington, DC, U.S., 2011.
[2]. *Annual Energy Outlook 2013 with Projections to 2040.* U.S. Department of Energy, U.S. Energy Information Administration, Office of Integrated and International Energy Analysis, Washington, 2013;
http://www.eia.gov/forecasts/aeo/pdf/0383(2013).pdf
[3]. Van Den Bossche, P.; Vergels, F.; Van Mierlo, J.; Matheys, J.; Van Autenboer, W. SUBAT: An assessment of sustainable battery technology. *J. Power Sources.* 2006, 162, 913–919.
[4]. Zackrisson, M.; Avellan, L.; Orlenius, J. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles---critical issues. *J. Cleaner Production.* 2010, 18, 1519-1529.
[5]. Notter, D. A.; Gauch, M.; Widmer, R.; Wager, P.; Stamp, A.; Zah, R.; Althaus, H.-J. Contribution of Li-ion batteries to the environmental impact of electric vehicles. *Environ. Sci. Technol*. 2010, 44, 6550–6.
[6]. Majeau-Bettez, G.; Hawkins, T.R.; Stromman, A.H. Lief cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. *Environ. Sci. Technol.* 2011, 45, 4548-4554.
[7]. Nigge, K.-M. *Life Cycle Assessment of Natural Gas Vehicles: Development and Application of Site-dependent Impact Indicators*; Springer: Berlin, Germany, 2000.
[8]. Aslam, M.U.; Masjuki, H.H.; Kalam, M.A.; Abdesselam, H.; Mahlia, T.M.I.; Amalina, M.A. An experimental investigation of CNG as an alternative fuel for a retrofitted gasoline vehicle. *Fuel.* 2006, 85, 717-724.
[9].Collantes, G.; Melaina, M.W. The co-evolution of alternative fuel infrastructure and vehicles: a study of the experience of Argentina with compressed natural gas. *Energ. Policy*. 2011, 39, 664-675.
[10].Pastorello, C.; Dilara, P.; Martini, G. Effect of a change towards compressed natural gas vehicles on the emissions of the Milan waste collection fleet. *Transpot. Res. D-TR. E.* 2011, 16, 121-128.
[11].Hesterberg, T.W.; Lapin, C.A.; Bunn, W.B. A comparison of emissions from vehicles fueled with diesel or compressed natural gas. *Environ. Sci. Technol.* 2008, 42, 6437-6445.
[12].Semin, R.A.B. A technical review of compressed natural gas as an alternative fuel for internal combustion engines. *Am. J. Engg. Appl. Sci.* 2008, 1, 302-311.
[13]. Hussain, M.M.; Dincer, I.; Li, X. A preliminary life cycle assessment of PEM fuel cell powered automobiles. *Applied Thermal Eng.* 2007, 27, 2294-2299.
[14]. Granovskii, M.; Dincer, I.; Rosen, M.A. Life cycle assessment of hydrogen fuel cell and gasoline vehicles. *Int. J. Hydrogen Energy*. 2006, 31, 337-352.
[15]. Ally, J.; Pryor, T. Life-cycle assessment of diesel, natural gas and hydrogen fuel cell bus transportation systems. *J. Power. Sources.* 2007, 170, 401-411.
[16]. Pehnt, M. Life-cycle assessment of fuel cell stacks. *Int. J. Hydrogen Energ.*2001, 26, 91-101.
[17]. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model, Argonne National Laboratory;

https://greet.es.anl.gov/
[18]. *Average Fuel Efficiency of U.S. Light Duty Vehicles*. Research and Innovative Technology Administration, Bureau of Transportation Statistics; http://www.bts.gov/publications/national_transportation_statistics/html/table_04_23.html
[19]. *Light-Duty Vehicle, Light-Duty Truck, and Medium-Duty Passenger Vehicle – Tier 2 Exhaust Emission Standards.* US EPA; http://www.epa.gov/oms/standards/light-duty/tier2stds.htm
[20]. 2012 Civic Natural Gas: http://automobiles.honda.com/shop/civic-natural-gas.aspx?kwid=90614098&adgrpid=&ef_id=UvAXgQAABQrkB7@q:20140206185946:s
[21]. 2013 Nissan Leaf: http://www.nissanusa.com/electric-cars/leaf/?dcp=ppn.63023882.&dcc=0.240189300
[22]. Mitsubishi Motors Upcoming Vehicles: http://www.mitsubishicars.com/upcoming-vehicles
[23]. 2014 Mitsubishi i MiEV electric car gets massive price cut: http://www.treehugger.com/cars/2014-mitsubishi-i-miev-electric-car-gets-massive-price-cut-6130.html
[24]. All-Electric Vehicles: Compare Side-by-Side: http://www.fueleconomy.gov/feg/evsbs.shtml
[25]. Honda FCX Clarity Overview: http://automobiles.honda.com/fcx-clarity/
[26]. 2015 Hyundai Tuscon Fuel Cell: https://www.hyundaiusa.com/tucsonfuelcell/
[27]. The B-Class F-Cell. Emission-free mobility with electric drive and fuel cell: http://www.mbusa.com/vcm/MB/DigitalAssets/pdfmb/fcell/248x168_b-klasse_f-cell_NP11_EN_DS_low2.pdf
[28]. 2012 Mercedes-Benz F-Cell: http://www.roadandtrack.com/car-reviews/first-drives/2012-mercedes-benz-f-cell
[29]. Lee, M.H.; Kang, Y.J.; Myung, S.T.; Sun, Y.k.. Synthsis optimization of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ via co-precipitation. *Electrochimica Acta*. 2004, 50, 939-948.
[30]. Todorov, Y.M.; Numata, K.. Effects of the Li: (Mn+Co+Ni) molar ratio on the electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material. *Electrochimica Acta*. 2004, 50, 495-499.
[31]. Application for Certification Civic GX: http://iaspub.epa.gov/otaqpub/display_file.jsp?docid=26868&flag=1
[32]. CNG Tanks (Cylinders) and Tank Mounting Brackets. Energy and Water Solutions (EWS): http://ewsews.com/tanks.php
[33]. Masten, D.A.; et al. System design for vehicle applications: GM/opel. In *Handbook of Fuel Cells: fundamentals, technology, and applications*; Vielstich, W. Eds.; John Wiley & Sons: New Jersey 2010.
[34]. *Cost Analysis of PEM Fuel Cell Systems for Transportation;* TIAX LLC: Cambridge, MA, 2005; http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/tiax_fc_cost_analysis_2005.pdf

[35]. *Life Cycle Assessment of a Natural Gas Combined-Cycle Power Generation System.* U.S. Department of Energy, National Renewable Energy Laboratory, Golden, CO, U.S., 2000.
http://www.nrel.gov/docs/fy00osti/27715.pdf

[36]. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming.* . U.S. Department of Energy, National Renewable Energy Laboratory, Golden, CO, U.S., 2001.
http://www-pord.ucsd.edu/~sgille/mae124_s06/27637.pdf

[37]. *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*; National Energy Technology Laboratory: Golden, CO, 2010: http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf

[38]. *HTGR-Integrated Hydrogen Production via Steam Methane Reforming (SMR) Process Analysis;* Idaho National Laboratory: Idaho Falls, ID, 2010; https://inlportal.inl.gov/portal/server.pt/document/78381/htgr-integrated_hydrogen_production_via_steam_methane_reforming_-smr-_economic_analysis_pdf

[39].*National Fuel Cell Electric Vehicle Learning Demonstration Final Report;* National Renewable Energy Laboratory: Golden, CO, 2012;
http://www.nrel.gov/hydrogen/pdfs/54860.pdf

[40].Annual Certification Test Results & Data, United States Environmental Protection Agency; http://www.epa.gov/otaq/crttst.htm

[41].Test Car List Data Files, United States Environmental Protection Agency;
http://www.epa.gov/otaq/tcldata.htm

[42]. Nukuda, T.; Inamasu, T.; Fujii, A.; Endo, D.; Nakagawa, H.; Kozono, S.; Iguchi, T.; Kuratomi, J.; Kohno, K.; Izuchi, S.; Oshitani, M.. Development of a lithium ion battery using a new cathode material. *J. Power Sources.*2005, 146, 611-616.

[43].Yamada, A.; Chung, S.C.; Hinokuma, K. Optimized $LiFePO_4$ for lithium battery cathodes. *J. Electrochem. Soc.* 2001, 148, A224-A229.

[44]. Garcia-Moreno, O.; Alvarez-Vega, M.; Garcia-Alvarado, E.; Garcia-Jaca, J.; Gallardo-Amores, J.M.; Sanjuan, M.L.; Amador, U.. Influence of the structure on the electrochemical performance of lithium transition metal phosphates as cathodic materials in rechargeable lithium batteries: a new high-pressure form of $LiMPO_4$ (M=Fe and Ni). *Chem. Mater.* 2001, 13, 1570-1576.

[45].Jang, M.W.; Jung, H.G.; Scrosati, B.; Sun, Y.K.. Improved co-substituted, $LiNi_{0.5-x}Co_{2x}Mn_{1.5-x}O_4$ lithium ion battery cathode materials. *J. Power Sources.*2012, 220, 354-359.

[46]. Omar, N.; Verbrugge, B.; Mulder, G.; Van den Bossche, P.; Van Mierlo, Joeri; Daowd, M.; Dhaens, M.; Pauwels, S.. Evaluation of performance characteristics of various lithium-ion batteries for use in BEV application. *Vehicle Power and Propulsion Conference (VPPC),* September 1-6, 2010.

[47]. Hohne, K.; Hirtz, E.. With system integratin and lightweight design to highest energy densities. *Advanced Microsystems for Automotive Application 2013*. Lecture Notes in Mobility 2013, 205-214.

[48]. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming;* National Renewable Energy Laboratory: Golden, CO, 2001;
http://www-pord.ucsd.edu/~sgille/mae124_s06/27637.pdf

[49]. Recently Tested Vehicles, Fuel Cell Vehicles;
http://www.fueleconomy.gov/feg/fcv_sbs.shtml
[50]. Chen, D.M.; Peng, H. A thermodynamic model of membrane humidifiers for PEM fuel cell humidification control. *J. Dtn. Control Syst.* 2005, 127, 425-432.
[51]. Singh, B.; Stromman, A.H.; Hertwich, E. Life cycle assessment of natural gas combined cycle power plant with post-combustion carbon capture, transport and storage. *Int. J. Greenh. Gas Con.* 2011, 5, 457-466.
[52]. IEA Energy Technology Essentials: CO_2 Capture and Storage, 2006:
http://www.iea.org/techno/essentials1.pdf
[53]. Solieman, A.A.A.; Dijkstra, J.W.; Haije, W.G.; Cobden, P.D.; van den Brink, R.W. Calcium oxide for CO_2 capture: Operational window and efficiency penalty in sorption-enhanced steam methane reforming. *Int. J. Greenh. Gas Con.* 2009, 3, 393-400.
[54]. Metz, B. Eds. *IPCC special report on carbon dioxide capture and storage;* Cambridge University Press: New York, 2005.
[55]. Khoo, H.H.; Tan, R.B.H. Life cycle investigation of CO_2 recovery and sequestration. *Environ. Sci. Technol.* 2006, 40, 4016-4024.
[56]. *Overview and Methodology*; ecoinvent report No. 1. Swiss Centre for Life Cycle Inventories: Dübendorf, Switzerland, 2007.
[57]. Goedkoop, M.J.; Heijungs, R; Huijbregts, M.; De Schryver, A.;Struijs, J.; Van Zelm, R. *ReCiPe 2008, A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level; First edition Report I: Characterisation*. May 2013:
http://www.lcia-recipe.net
[58]. *Platinum Group Metal Recycling Technology Development;* BASF Catalysts LLC: Iselin, NJ, 2009; http://www.osti.gov/bridge/servlets/purl/962699-ivryK6/962699.pdf.
[59]. Li, L.; Ge, J.; Wu, F.; Chen, R.J.; Chen, S.; Wu, B.R. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J. Hazard. Mater.* 2010, 176, 288-293.

4.4 Supporting Information

4.4.1 System boundary and description

The system boundary of this study is shown in Figure 4-1. It starts with natural gas extraction, and ends with natural gas-propelled miles delivered by CNGV, BEV and FCV. For the three natural gas utilization pathways, vehicle manufacturing and assembly, as well as infrastructure to convert natural gas to vehicle specific fuel is included as part of the material processing and manufacturing life cycle stages. For BEV and FCV, carbon capture at the fuel processing facilities is considered when modeling infrastructure, while recycling of the batteries is included to present the end-of-life stages. The cut-off criteria is set to be 1%, suggesting processes and material/energy inputs whose contributions to the total environmental is less than 1% will not be included in the analysis.

4.4.2 Life cycle inventories

4.4.2.1 Reference ICEV

The LCI for ICEV is adapted from the LCI reported in literature[1]. U.S. gasoline is not available from the Ecoinvent database, so the LCI of gasoline at the refinery was taken from the USLCI database, while the material and energy inputs from the refinery to regional storage were assumed to be the same as the case of European average. For the operation, it’s assumed that the ICEV meets the CAFÉ standards for 2010[2] and the EPA tier 2 emission standards[3]. The use phase LCI showing major emissions is given in Table S4-1.

4.4.2.2 CNGV

4.4.2.2.1 Vehicle manufacturing

A compressed natural gas tank is the most distinctive part of CNGV compared with ICEV. In this study, we assumed a 100 kg chrome steel tank based on information obtained from CNGV tank manufacturer[4]. For other vehicle parts, CNGV is assumed to have the same configuration as gasoline based ICEV.

Table S4-17. LCI of ICEV operation

Products		
Operation, passenger car, petrol, EPA tier 2/US U	1	km
Materials/fuels		
Petrol, low-sulphur, at regional storage/US U	0.061558	kg
Emissions to air		
Carbon dioxide, fossil	0.1901	kg
Sulfur dioxide	3.69E-06	kg
Carbon monoxide, fossil	0.00261	kg
Nitrogen oxides	4.35E-05	kg
Particulates, > 10 um	8.96E-05	kg
Particulates, > 2.5 um, and < 10um	1.55E-05	kg
Particulates, < 2.5 um	9.73E-06	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	0.000107	kg

Table S4-18. LCI of CNGV operation

Products		
Operation, dedicated CNG, Civic GX/US U	1	km
Materials inputs		
Natural gas, from high pressure network (1-5 bar), at service station/CH U	0.05022	kg
Energy inputs		
Electricity, medium voltage, at grid/US U	0.015	kWh
Emissions to air		
Carbon dioxide, fossil	0.133862	kg
Sulfur dioxide	0.0015	g
Carbon monoxide, fossil	0.287695	g
Nitrogen oxides	0.003045	g
Particulates, > 2.5 um, and < 10um	0.011	g
NMVOC, non-methane volatile organic compounds, unspecified origin	0.001305	g

4.2.2.2.2 Use phase

Fuel economy and emissions of CO_2, CO, NO_x and non-methane organic compounds are retrieved from EPA's annual vehicle test database[5-6] for a 2010 Honda Civic GX, which is one of the few CNGVs available on the U.S. market. Other emissions from CNGV is assumed to be the same as that from ICEV. The LCI of CNGV operation is given in Table S4-2.

4.2.2.2.3 Infrastructure

The infrastructure is represented by a fueling station. Again, the configuration is assumed to be the same as a gasoline fuel station. Additional energy to compress natural gas at the fueling station is taken from Collantes, 2011[7]. This electricity consumption is included in the operation LCI.

4.2.2.3 BEV

4.2.2.3.1 Vehicle Manufacturing

The drive train and glider LCI is adapted from that reported by Notter *et al.*[1] For the LIB pack, the active material is NCM. The LCI of NCM production is based on a co-precipitation synthesis method reported in literature[8]. Composition of single LIB cell is taken from battery design studio for a he18650 cell. LCIs of LIB manufacturing are presented in Table S4-3 and S4-4.

Table S4-19. LCI of NCM Precursor Synthesis

Products		
Ni1/3Co1/3Mn1/3(OH)2	1	kg
Materials inputs		
MnSO4 2M solution	5.746	l
NiSO4 2M solution	5.746	l
CoSO4 2M solution	5.746	l
Sodium hydroxide 6M solution	3.829	l
Ammonia aqueous solution, saturated	1	l
Water, deionised, at plant/CH U	1	kg
Energy inputs		
Heat, natural gas, at industrial furnace >100kW/RER U	0.232	MJ
Electricity, medium voltage, at grid/CN U	0.005	kWh

Table S4-4. LCI of NCM synthesis

Products		
NCM, co-precipitation	1	kg
Materials inputs		
Lithium hydroxide, at plant/GLO U	0.2615	kg

Ni1/3Co1/3Mn1/3(OH)2	0.9982	kg
Oxygen, liquid, at plant/RER U	0.0872	kg
Energy inputs		
Electricity, medium voltage, at grid/CN U	0.005	kWh
Heat, natural gas, at industrial furnace >100kW/RER U	21.388	MJ
Transport, freight, rail/RER U	0.7733	tkm
Transport, lorry >16t, fleet average/RER U	0.1347	tkm

As for the assembly of LIB pack, dry room is the single largest energy consumer during the assembly stage.[9] Electricity and natural gas consumption of dry room operation, equal to 0.0088kWh/cell and 0.058MJ/cell respectively, were estimated based on annual consumption provided by the dry room manufacturer.[10] Natural gas and electricity consumption for LIB assembly is then calculated assuming that dry room operation and accounts for 60% of the electricity consumption of the manufacturing facility. Material inputs for the LIB assembly is obtained from literature.[1, 11] LCIs relevant to the assembly stage are listed in Table S4-5 and 4-6.

4.2.2.3.2 Use phase

Electricity consumption by BEV is computed using vehicle simulation program (VSP).[12] It accounts for the additional energy required to haul the battery pack. VSP requires information on energy density, battery mass and average energy efficiency of the LIB cell. Since LIB cell deteriorates as it undergoes more charge-discharge cycles, besides energy density, another electrochemical property, which is cycle life, is needed to estimate average energy efficiency. Energy density and cycle life of NCM is retrieved from average value reported in literature.[13-18] In this study, energy stored in the LIB pack is assumed to be 40 kWh[19], so battery mass can be calculated once we know the energy density. Assuming an 80% depth of discharge, and a 10% charging loss, electricity consumption per mile driven can be calculated using VSP. The operation of BEV is assumed to be emission free.

Table S4-5. LCI of LIB single cell

Products		
LIB single cell	1	p
Materials inputs		

Active cathode material	12.3942	g
Graphite, battery grade, at plant/CN U	8.0976	g
Lithium hexafluorophosphate, at plant/CN U	0.6762	g
Carbon black, at plant/GLO U	0.6825	g
Ethylene carbonate, at plant/CN U	4.3344	g
Polyvinylfluoride film, at plant/US U	1.1823	g
Polyethylene terephthalate, granulate, bottle grade, at plant/RER U	0.441	g
Polyethylene, LDPE, granulate, at plant/RER U	0.7287	g
Steel, electric, chromium steel 18/8, at plant/RER U	9.03	g
Cathode, copper, primary copper production/GLO U	3.62565	g
Aluminium, primary, at plant/RER U	1.77975	g
Energy inputs		
Transport, freight, rail/RER U	0.0191	tkm
Transport, lorry >16t, fleet average/RER U	0.0043	tkm

Table S4-6. LCI of LIB cell assembly into LIB pack

Products		
cell assembly, U/US	1	p
Materials inputs		
Integrated circuit, IC, logic type, at plant/GLO U	0.01	g
Water, deionised, at plant/CH U	6.707	g
Aluminium, primary, at plant/RER U	7.2	g
Nickel, 99.5%, at plant/GLO U	0.045	g
Cable, data cable in infrastructure, at plant/GLO U	0.018	m
Steel, electric, chromium steel 18/8, at plant/RER U	0.1	g
Energy inputs		
Electricity, medium voltage, at grid/US U	0.015	kWh
Natural gas, burned in industrial furnace >100kW/RER U	0.07	MJ
Sheet rolling, aluminium/RER U	8.97975	g
Sheet rolling, copper/RER U	3.62565	g
Sheet rolling, chromium steel/RER U	9.03	g
Injection moulding/RER U	1.1697	g
Transport, lorry >16t, fleet average/RER U	0.0014	tkm
Transport, freight, rail/RER U	0.0056	tkm

4.2.2.3.3 Infrastructure

Infrastructure associated with the BEV pathway is represented by a NGCC power plant. Material and energy flow is taken from literature[20], assuming a 50.2% thermal efficiency without carbon capture, and a 7.5% energy penalty for carbon capture. For the scenario with carbon capture, We obtain from Singh *et al* (2011)[21] values of MEA, NaOH, activated carbon consumptions, and MEA, ammonia, formaldehyde, acetaldehyde emissions. LCIs showing major material and energy input/output are given is Table S4-7 and 4-8.

Table S4-7. LCI of 1kwh electricity produced at NCGG plant

Products		
Electricity, at NGCC plant 2010 /US U	1	kWh
Material inputs		
Natural gas, burned in NGCC plant 2010/US U	7.172	MJ
Ammonia, liquid, at regional storehouse/RER U	0.175	g
Water, decarbonised, at plant/RER U	0.746	kg
Energy inputs		
Transport, crude oil pipeline, onshore/RER U	0.000746	tkm
Transport, freight, rail/RER U	0.000105	tkm
Transport, lorry >16t, fleet average/RER U	1.75E-05	tkm

Table S4-8. LCI of 1kwh electricity produced at NGCC plant with carbon capture

Products		
Electricity, at NGCC plant w/CC 2010 /US U	1	kWh
Materials inputs		
Natural gas, burned in NGCC plant w/CC 2010/US U	8.411	MJ
Ammonia, liquid, at regional storehouse/RER U	0.175	g
Water, decarbonised, at plant/RER U	1.432	kg
Monoethanolamine, at plant/RER U	0.5805	g
Sodium hydroxide, 50% in H2O, production mix, at plant/RER U	0.1	g
Charcoal, at plant/GLO U	0.029	g
Energy inputs		
Transport, freight, rail/RER U	0.000531	tkm
Transport, lorry >16t, fleet average/RER U	8.85E-05	tkm
Transport, crude oil pipeline, onshore/RER U	0.001432	tkm
Emissions to air		
Carbon dioxide	43	g
Ammonia	0.0135	g
Formaldehyde	0.000101	g
Acetaldehyde	6.46E-05	g
Nitrogen oxides	0.027	g
Monoethanolamine	0.0244	g

4.2.2.3.4 End-of-Life

Spent LIB is assumed to be recycled via hydrometallurgical process[22]. LCI is presented in Table S4-9.

Table S4-9. LCI of recycling 1 kg spent LIB by hydrometallurgical process

Material inputs		
	Value	Unit
Spent LIB	1	kg
NMP	0.14	g
Citric acid	0.952	kg
H_2O_2	0.174	kg
water	1.2	kg
Energy inputs		
	Value	Unit
Electricity	0.351	kWh
Natural gas	1.485	MJ
Transportation, rail	3.152484	tkm
Transportation, road	0.525414	tkm
Material outputs		
	Value	Unit
Lithium citrate	0.485	kg
Cobalt citrate	0.972	kg
Graphite	64	g
Aluminum	75.6	g
Copper	31	g
Steel	126	g
Emissions		
	Value	Unit
CO_2	85.4	g

4.2.2.4 FCV

4.2.2.4.1 Vehicle Manufacturing

FCV is supposed to have the same power train and glider configuration as BEV. For the 20 KW LIB, it's assumed that it meets the USABC power density goal of 400W/kg[19], which yields a 50 kg LIB pack based on NCM. The 80 KW PEMFC consists of the fuel cell stack and balance of plants. Composition of fuel cell stack is obtained from a cost report[23]. Balance of plant consists of fuel delivery sub-system, air delivery sub-system and water and thermal management sub-system[24]. Water and thermal management sub-system is represented by the cooling system adopted in the BEV drivetrain. Fuel delivery sub-system is represented by the fuel injection system used in the ICEV drivetrain. Air delivery sub-system is represented by the air intake system deployed in the ICEV drivetrain, in addition to an air compressor and a deionized water-fed membrane humidifier. The hydrogen storage tank is assumed to be a 17 kg type IV carbon fiber tank[25]. LCIs of PEMFC are given in Table S4-10~4-12.

Table S4-10. LCI of graphite bipolar plate

Products		
Graphite foil bipolar plate	1	kg
Materials/fuels		
Polyester resin, unsaturated, at plant/RER U	0.15	kg
Graphite, battery grade, at plant/US	0.81	kg
Acrylonitrile from Sohio process, at plant/RER U	0.294	kg
Methyl ethyl ketone, at plant/RER U	0.0818	kg
Hydrogen peroxide, 50% in H2O, at plant/RER U	0.0773	kg

Table S4-11. LCI of balance of plant

Products		
PEM BOP	1	p
Materials/fuels		
Steel, low-alloyed, at plant/RER U	2.5	kg
Reinforcing steel, at plant/RER U	43.5	kg
Aluminium, production mix, at plant/RER U	2.5	kg
Polyphenylene sulfide, at plant/GLO U	5.5	kg
Synthetic rubber, at plant/RER U	1	kg
Tetrafluoroethylene film, on glass/RER U	0.4568	kg
Transport, lorry >16t, fleet average/RER U	5.5457	tkm
Transport, freight, rail/RER U	13.874	tkm

Table S4-12. LCI of PEMFC

Products		
Battery,PEM 80 KW, at plant/GLO U	1	p
Materials/fuels		
Platinum, at regional storage/RER U	0.1	kg
Carbon black, at plant/GLO U	0.459	kg
Electricity, medium voltage, at grid/US U	60	kWh
Transport, lorry >16t, fleet average/RER U	4.3836	tkm
Heat, natural gas, at industrial furnace >100kW/RER U	280	MJ
Acrylonitrile from Sohio process, at plant/RER U	10.434	kg
Graphite foil bipolar plate	29.5495	kg
Natural rubber based sealing, at plant/DE U	1.5338	kg
Tetrafluoroethylene film, on glass/RER U	1.497	kg
Transport, freight, rail/RER U	26.3018	tkm
Tetrafluoroethylene, at plant/RER U	0.263	kg
PEM BOP	1	p

Emissions to air		
Heat, waste	360	MJ

4.2.2.4.2 Use phase

Hydrogen consumption for FCV is estimated from values in the NREL 2012 report[26]. An average fuel economy of 50 miles per gallon is assumed for FCV. No emissions is assumed for the operation of FCV.

Table S4-13. LCI of 1kg H2 production at SMR plant

Products		
H2 SMR conventional, US/U	1	kg
Avoided products		
Steam, for chemical processes, at plant/RER U	6.4	kg
Materials/fuels		
Natural gas, production mix, at service station/CH U	3.5	kg
Water, decarbonised, at plant/RER U	16.42	kg
Electricity, medium voltage, at grid/US U	0.483	kWh
Emissions to air		
Carbon dioxide, fossil	9.29	kg
Carbon monoxide, fossil	0.0798	g
Nitrogen oxides	0.898	g
Particulates	0.022	g

4.2.2.4.3 Infrastructure

Infrastructure for FCV involves a SMR plant. LCI for production of hydrogen (Table S4-13 and 4-14) from SMR process with and without carbon capture is based on the INL 2010 report[27]. Additional energy, 4.8 kwh/kg hydrogen[26], is assumed for the further compression.

Table S4-14. LCI of 1kg H2 production with carbon capture

Products		
H2 SMR with carbon capture, US/U	1	kg
Avoided products		
Steam, for chemical processes, at plant/RER U	0.8	kg
Materials/fuels		

Natural gas, production mix, at service station/CH U	3.28	kg
Water, decarbonised, at plant/RER U	11.31	kg
Monoethanolamine, at plant/RER U	10.32	g
Electricity, medium voltage, at grid/US U	1.104	kWh
Emissions to air		
Carbon dioxide, fossil	2.478	kg
Carbon monoxide, fossil	0.0798	g
Nitrogen oxides	0.898	g
Particulates	0.022	g

Table S4-15. LCI for CO2 pipeline

Products		
CO2 pipeline to injection well, 300km	1	p
Materials/fuels		
Reinforcing steel, at plant/RER U	60.6	kton
Gravel, unspecified, at mine/CH U	67.8	kton
Cement, unspecified, at plant/CH U	12	kton
Aluminium, production mix, at plant/RER U	333	ton
Zinc, primary, at regional storage/RER U	17.4	ton
Copper, at regional storage/RER U	21	kg
Diesel, burned in building machine/GLO U	253.8	MJ
Electricity, medium voltage, at grid/US U	9600	MWh

Same sequestration process is assumed for carbon captured at the NGCC plant and the SMR plant. LCI for CO_2 pipeline (Table S4-15), assuming a length of 300 km[28], as well as LCI of the injection well (Table S4-16), is taken from Singh *et al* (2011)[21]. While energy consumption for pipeline transportation, and recompression and injection at the injection well is obtained from Khoo et al (2006)[29].

Table S4-16. LCI of infection well

Products		
CO2 injection well	1	p
Materials/fuels		
Reinforcing steel, at plant/RER U	168	ton
Barite, at plant/RER U	216	ton
Bentonite, at processing/DE U	16	ton
Portland calcareous cement, at plant/CH U	160	ton
Chemicals inorganic, at plant/GLO U	41	ton
Lubricating oil, at plant/RER U	48	kg
Diesel, burned in building machine/GLO U	14.4	GJ

4.2.2.4.4 End-of-Life

Spent PEMFC is recycled to recover platinum based on commercially available technology[30]. The LCI is represented in Table S4-17.

Table S4-17. LCI of recycling 1 kg spent PEMFC

Products		
PEM FC recycling, acid leaching	1	kg
Avoided products		
Platinum, at regional storage/RER U	0.992	g
Materials/fuels		
Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER U	0.2412	kg
Nitric acid, 50% in H2O, at plant/RER U	0.094	kg
Sodium hydroxide, production mix, at plant/kg/RNA	0.084	kg
Urea, as N, at regional storehouse/RER U	0.00327	kg
Propylene glycol, liquid, at plant/RER U	0.001	kg
Nitrogen, liquid, at plant/RER U	0.145	kg
Electricity, medium voltage, at grid/US U	0.539	kWh
Transport, freight, rail/RER U	0.2818	tkm
Transport, lorry >16t, fleet average/RER U	0.05685	tkm

4.4.3 Monte Carlo Simulation

Based on the mean, variance and distribution type for each technology parameter listed in Table 4-1, Monte Carlo simulation is conducted in MATLAB. 10,000 realizations are simulated for each life cycle impact assessment method, with random selection of technology parameters for each realization. Sample MATLAB code is as follows:

```
clear all
format short

number=10000; %number of realizations

%Manufacturing phase excluding battery
CNGVM=7.45;
BEVM=7.31;
FCEVM=7.31;

%mu = log(mean(y)) - 1/2*log(1 + var(y)/(mean(y))^2);
%sigma = sqrt( log( 1 + var(y)/(mean(y))^2) );
for i=1:number
    %BEV battery uncertainty
```

```
    NCMSE(i)=randraw('lognorm',[4.90472638,0.03311785]);
    NCMCL(i)=randraw('lognorm',[7.17,0.0153837]);
    %FCEV battery uncertainty
    FCPt(i)=randraw('lognorm',[-1.0873759,0.88795122]);
    %CNGV tank uncertainty
    CNGVTmass(i)=randraw('lognorm',[4.6041712,0.044699]);
    %Fuel economy uncertainty
    CNGVFE(i)=randraw('lognorm',[3.4288112,0.1017451]);
    FCEVFE(i)=randraw('lognorm',[3.91002699,0.06318244]);
    %NGPP SMRP thermal efficiency
    NGPPTE(i)=randraw('lognorm',[3.80542944,0.04965977]);
    SMRTE(i)=randraw('lognorm',[4.38124599,0.03951204]);

    %CNGV
    CNGVT(i)=0.00386*CNGVTmass(i);
    UseCNGV(i)=0.288/1000*31/CNGVFE(i)*120000;
    CNGV(i)=CNGVM+CNGVT(i)+UseCNGV(i);

    %BEV NCM
    MassBNCM(i)=40000/NCMSE(i);
    CnumNCM(i)=ceil(MassBNCM(i)/0.05);
    N_bat(i)=ceil(1000/NCMCL(i));
    PackNCM(i)=0.000563*CnumNCM(i)*N_bat(i);
    RangeNCM(i)=0.8*NCMSE(i)*MassBNCM(i)*0.9/(MassBNCM(i)*0.054+133)/1.609344;
    ENCM(i)=40*1.1/RangeNCM(i);
    UseNCM(i)=0.3732*(0.0649*3.6/NGPPTE(i)*100*1.05+0.0004)*120;
    BEVNCM(i)=BEVM+PackNCM(i)+UseNCM(i);

    %FCEV
    PEM(i)=FCPt(i)/0.75*1.48+1.73;
    MassLIB=20/0.5;
    FCLIB=MassLIB/0.05*0.000335;
    FCB(i)=PEM(i)+FCLIB;
    UseFC(i)=0.02*(72/SMRTE(i)*2.07+9.29+0.373-1.5)*120;
    FCEV(i)=FCEVM+FCB(i)+UseFC(i);

end
```

GWP results from three Monte Carlo Simulations based on different numbers of realizations are summarized in Table S4-18. The results suggest that 10,000 realizations are sufficient for the results to be reproducible within a range of ±1%.

Table S4-18. Summary of GWP Results in ton CO_2 eq. from Different Numbers of Monte Carlo Realizations

		10000 realizations			1000 realizations			100 realizations		
		Mean	Upper	Lower	Mean	Upper	Lower	Mean	Upper	Lower
Total	CNGV	42.39	53.92	37.00	42.38	54.09	36.99	42.56	52.45	36.99
	BEV	31.71	37.13	27.84	31.66	37.43	27.96	31.98	36.94	27.50
	BEV CCS	18.01	22.45	16.38	18.04	22.74	16.32	18.12	22.80	16.32
	FCV	42.01	50.56	36.47	42.14	51.12	36.35	41.21	49.58	36.88

	FCV CCS	30.63	36.22	27.07	30.72	36.28	27.06	30.25	35.76	27.05
Exclusive parts	Tank	0.45	0.62	0.27	0.45	0.62	0.28	0.46	0.59	0.30
	LIB	3.49	7.76	2.57	3.51	8.02	2.55	3.40	7.79	2.58
	PEMFC	2.27	3.01	1.75	2.28	3.01	1.75	2.26	3.03	1.74
Use	CNGV	36.26	47.80	30.87	36.29	48.05	30.83	36.40	46.21	30.81
	BEV	22.71	26.66	19.47	22.61	26.54	19.52	22.96	26.78	19.37
	BEV CCS	9.23	10.43	8.26	9.20	10.40	8.26	9.30	10.43	8.21
	FCV	34.50	43.08	29.04	34.70	43.68	28.88	33.82	41.32	29.25
	FCV CCS	23.14	28.64	19.68	23.29	28.87	19.62	22.81	27.64	19.83

4.4.4 Additional LCIA results

Compared to $LiMn_2O_4$ (LMO), NCM has not been used extensively in BEV applications. In this study, NCM was chosen as the LIB cathode active material because it represents an active area of near-term technology development for BEVs. However, since commercial scale LIB performance parameters are available for the LMO cathode chemistry, the environmental impacts of natural gas powered mobility using BEVs powered by LMO LIBs were also evaluated. The results in comparison to BEVs powered with NCM LIBs are shown in Figure S1.

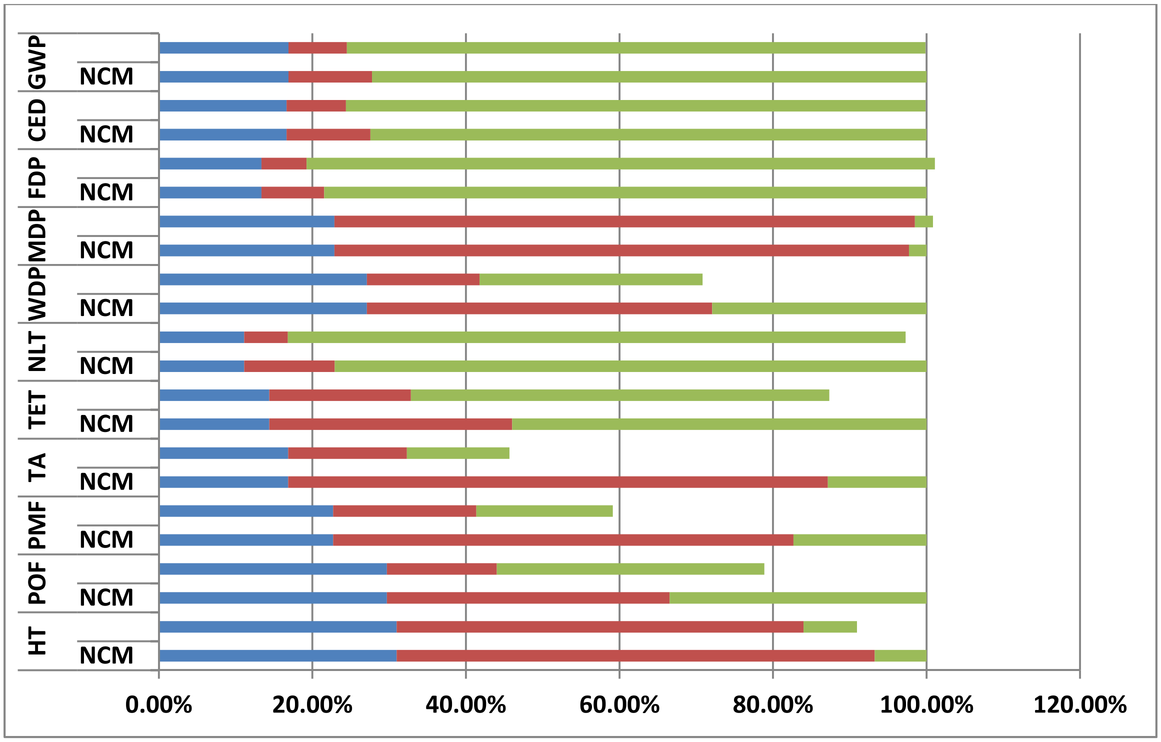

Figure S4-7. LCIA comparison of LMO-based BEV and NCM-based BEV, normalized to NCM-based BEV. Again, blue bars represent glider and powertrain; red bars represent power source; green bars represent use phase.

The LMO LIB electrochemical properties are as follows[30-33]: average specific energy of 115 Wh/kg, and cycle life of 1000.

Additional LCIA results for carbon capture and storage for the NGCC plant and the SMR plant are presented in Figures S4-2.

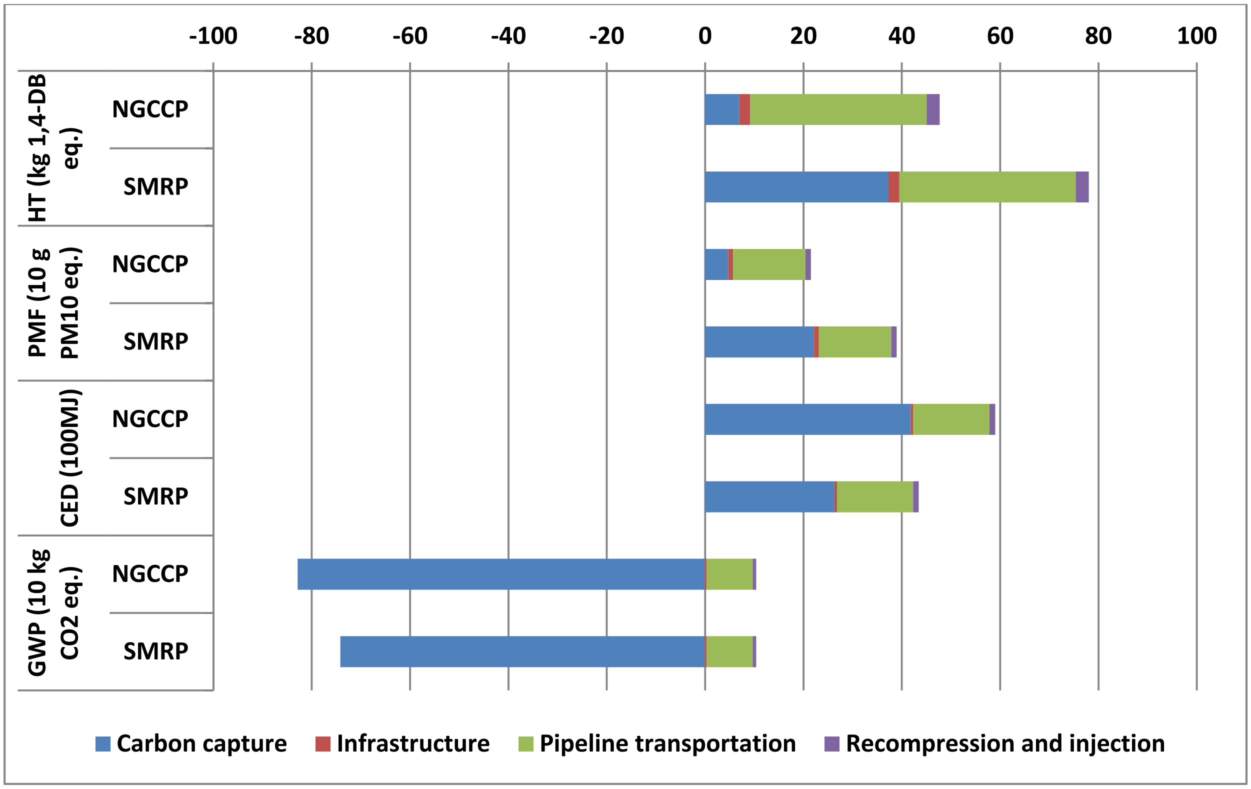

Figure S4-8. Environmental Impacts Break-down for CCS at NGCC plant and SMR plant

References

[1]. Notter, D. A.; Gauch, M.; Widmer, R.; Wager, P.; Stamp, A.; Zah, R.; Althaus, H.-J. Contribution of Li-ion batteries to the environmental impact of electric vehicles. *Environ. Sci. Technol*. 2010, 44, 6550–6.
[2]. *Average Fuel Efficiency of U.S. Light Duty Vehicles*. Research and Innovative Technology Administration, Bureau of Transportation Statistics; http://www.bts.gov/publications/national_transportation_statistics/html/table_04_23.html
[3]. *Light-Duty Vehicle, Light-Duty Truck, and Medium-Duty Passenger Vehicle – Tier 2 Exhaust Emission Standards.* US EPA; http://www.epa.gov/oms/standards/light-duty/tier2stds.htm
[4]. CNG Tanks (Cylinders) and Tank Mounting Brackets. Energy and Water Solutions (EWS): http://ewsews.com/tanks.php

[5]. Annual Certification Test Results & Data, United States Environmental Protection Agency; http://www.epa.gov/otaq/crttst.htm
[6]. Test Car List Data Files, United States Environmental Protection Agency; http://www.epa.gov/otaq/tcldata.htm
[7]. Collantes, G.; Melaina, M.W. The co-evolution of alternative fuel infrastructure and vehicles: a study of the experience of Argentina with compressed natural gas. *Energ. Policy.* 2011, 39, 664-675.
[8]. Lee, M.H.; Kang, Y.J.; Myung, S.T.; Sun, Y.k.. Synthsis optimization of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ via co-precipitation. *Electrochimica Acta*. 2004, 50, 939-948.
[9]. Dunn, J.B.; Gaines, L.; Barnes, M.; Sullivan, J.; Wang, M. *Material and energy flows in the materials production, assembly, and end-of-life stages of the automotive Lithium-ion battery life cycle*. Center for Transportation Research, Energy System Division, Argonne National Laboratory, Illinois, U.S., 2012.
[10]. *Advanced dry room concepts*, Harris Environmental Systems; http://www.harris-env.com/korea_paper.htm
[11]. Majeau-Bettez, G.; Hawkins, T.R.; Stromman, A.H. Lief cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. *Environ. Sci. Technol.* 2011, 45, 4548-4554.
[12]. Mierlo, J.V. and Maggetto, G. Innovative iteration algorithm for a vechile simulation program. *IEEE T. Veh. Tech.* 2004, 53, 401-412.
[13]. Nukuda, T.; Inamasu, T.; Fujii, A.; Endo, D.; Nakagawa, H.; Kozono, S.; Iguchi, T.; Kuratomi, J.; Kohno, K.; Izuchi, S.; Oshitani, M.. Development of a lithium ion battery using a new cathode material. *J. Power Sources.*2005, 146, 611-616.
[14]. Yamada, A.; Chung, S.C.; Hinokuma, K. Optimized $LiFePO_4$ for lithium battery cathodes. *J. Electrochem. Soc.* 2001, 148, A224-A229.
[15]. Garcia-Moreno, O.; Alvarez-Vega, M.; Garcia-Alvarado, E.; Garcia-Jaca, J.; Gallardo-Amores, J.M.; Sanjuan, M.L.; Amador, U.. Influence of the structure on the electrochemical performance of lithium transition metal phosphates as cathodic materials in rechargeable lithium batteries: a new high-pressure form of $LiMPO_4$ (M=Fe and Ni). *Chem. Mater.* 2001, 13, 1570-1576.
[16]. Jang, M.W.; Jung, H.G.; Scrosati, B.; Sun, Y.K.. Improved co-substituted, $LiNi_{0.5-x}Co_{2x}Mn_{1.5-x}O_4$ lithium ion battery cathode materials. *J. Power Sources.*2012, 220, 354-359.
[17]. Omar, N.; Verbrugge, B.; Mulder, G.; Van den Bossche, P.; Van Mierlo, Joeri; Daowd, M.; Dhaens, M.; Pauwels, S.. Evaluation of performance characteristics of various lithium-ion batteries for use in BEV application. *Vehicle Power and Propulsion Conference (VPPC),* September 1-6, 2010.

[18]. Hohne, K.; Hirtz, E.. With system integratin and lightweight design to highest energy densities. *Advanced Microsystems for Automotive Application 2013*. Lecture Notes in Mobility 2013, 205-214.
[19]. USABC Goals for Advanced Batteries for EVs, United States Council for Automotive Research LLC;
http://www.uscar.org/guest/article_view.php?articles_id=85;
[20]. *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*; National Energy Technology Laboratory: Golden, CO, 2010:
http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf
[21]. Singh, B.; Stromman, A.H.; Hertwich, E. Life cycle assessment of natural gas combined cycle power plant with post-combustion carbon capture, transport and storage. *Int. J. Greenh. Gas Con.* 2011, 5, 457-466.
[22]. Li, L.; Ge, J.; Wu, F.; Chen, R.J.; Chen, S.; Wu, B.R. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J. Hazard. Mater.* 2010, 176, 288-293.
[23]. *Cost Analysis of PEM Fuel Cell Systems for Transportation;* TIAX LLC: Cambridge, MA, 2005;
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/tiax_fc_cost_analysis_2005.pdf
[24]. Masten, D.A.; et al. System design for vehicle applications: GM/opel. In *Handbook of Fuel Cells: fundamentals, technology, and applications*; Vielstich, W. Eds.; John Wiley & Sons: New Jersey 2010.
[25]. Gas storage, Material Hydrogen Technology:
http://www.mahytec.com/en/hpstorage.html
[26]. *National Fuel Cell Electric Vehicle Learning Demonstration Final Report;* National Renewable Energy Laboratory: Golden, CO, 2012;
http://www.nrel.gov/hydrogen/pdfs/54860.pdf
[27]. HTGR-Integrated Hydrogen Production via Steam Methane Reforming (SMR) Process Analysis; Idaho National Laboratory: Idaho Falls, ID, 2010;
https://inlportal.inl.gov/portal/server.pt/document/78381/htgr-integrated_hydrogen_production_via_steam_methane_reforming_-smr-_economic_analysis_pdf
[28]. Metz, B. Eds. *IPCC special report on carbon dioxide capture and storage;* Cambridge University Press: New York, 2005.
[29]. Khoo, H.H.; Tan, R.B.H. Life cycle investigation of CO_2 recovery and sequestration. *Environ. Sci. Technol.* 2006, 40, 4016-4024.
[30]. *Platinum Group Metal Recycling Technology Development;* BASF Catalysts LLC: Iselin, NJ, 2009;
http://www.osti.gov/bridge/servlets/purl/962699-ivryK6/962699.pdf

Chapter 5

Incorporating Technological Progression and Policy into Life Cycle Assessment: Case Study of Personal Passenger Vehicles

5.1 Introduction

Life cycle assessment (LCA) is a useful tool to evaluate the environmental impacts of a product or service over its lifetime. In the past decade, LCA became popular in environmental policymaking, green manufacturing and eco-design. However, traditional LCA has its limitations. Reap *et al* (2008) looked into unresolved problems in LCA, and summarized severity and sufficiency of current remedies of each problem. They especially pointed out that the assumption of global homogeneity and steady-state conditions is responsible for the most severe errors in LCA.

Being unable to address spatial and temporal variations has long been known as one of the major limitations of traditional LCA. In recent years, numerous studies have emerged to tackle these two problems. Azevedo *et al* (2013) assessed the significance of spatial variations in LCA. Gasol *et al* (2011) and Dresen *et al* (2012) incorporated spatial modeling into LCA with geoinformation systems. Levasseur *et al* (2010) and Kendall (2012) recognized the dynamic pattern of the greenhouse gas emissions over the lifetime of long-lasting products, and investigated its effect on the impact assessment of global warming potential. Yuan *et al* (2009) employed a discounting method to emissions of

VW Golf A4 in a case study. Stasinopoulos *et al* (2012) also focused on the temporal effects of material use on energy flows for cars.

These research efforts point the LCA community to a new direction with regard to methodology development. However, among current studies to account for temporal variations, the common practice is to apply a surrogate discount rate to life cycle inventory (LCI) entries to reflect possible future technology advance, without a quantitative representation of how technological progression would actually change the LCI. This research is an attempt to bridge this gap by translating technological progression forecasting into time-adjusted LCI.

Technological progression modeling has been incorporated into recent research on energy and sustainability (Koh *et al* 2008, Haslam *et al* 2012, Tran *et al* 2012 and Leu *et al* 2012). It's capable of providing satisfying prediction of future technological performance metrics and can partly answer the question of where technology will lead us. In this study, we adopted the performance curve model as described by McNerney *et al* 2011, which is also known as Wright's law. We applied the model to the LCA of three types of passenger vehicles at different stages of technology diffusion: internal combustion engine vehicles (ICEVs) with a mature market, battery electric vehicles (BEVs) at the early adoption stage, and hydrogen fuel cell vehicles (FCVs) at the demonstration stage, hoping that the different paces of technology progression for the three vehicles would give us more insights into the effect of temporal variation on LCA. As vehicles are of long lifetime, and the use phase impacts dominate the lifecycle environmental burden (Notter *et al* 2010, Majeau-Bettez *et al* 2011), we also considered possible technology advance in fuel conversion technologies, especially for natural gas combined cycle

(NGCC) power plant to produce electricity for BEV, and steam methane reforming (SMR) plant to produce hydrogen for FCV.

In addition to technology improvement, future environmental policy and legislation could also affect the material and energy flows of the next generation of the three vehicles. In this study, we also incorporated CAFE standard for model years 2017-2025 cars and light trucks (DOT NHTSA, 2012) and EPA's National GHG Emission Standard for cars of the same model years (EPA, 2012).

5.2 Methods

Traditional LCA is firstly conducted on ICEV, BEV and FCV as the reference case (third paper). The functional unit is defined to be 120,000 miles driven over a 10-year lifetime. The LCIs of the three vehicles are then adjusted based on predicted technology parameters, using material and energy inputs obtained from Ecoinvent database 2.2. At the manufacturing and assembly stage, the effect of technology advance and environmental legislation is investigated by examining the environmental impacts of the three vehicles produced in 2010 and 2020 respectively. At the use phase, the continuous improvement in fuel conversion technology is accounted for using a time-series LCI. The thermal efficiency of the NGCC power plant and the SMR plant is retrieved on an annual basis over the 10 year lifetime of the vehicles, and the LCI entries of the vehicle operation for that year are updated correspondingly.

To model technological progress, Wright's law has been adopted:

$$\log y_t = a\, log x_t + b + n(t)$$

where y_t is the unit cost of the technology measured in inflation-adjusted dollars, x_t is the cumulative production, n(t) is the noise term, and a and b are constants specific to each technology. In this study, y_t actually represents performance metrics of a technology.

Historical technology performance data on lithium ion battery is found from the performance curve database maintained by Santa Fe Institute, while cumulative production and thermal efficiency of NGCC power plant are obtained from the electricity power annual of 2012 (EIA 2013). For the fuel cell in FCV, historical data of its performance is not available, so future fuel cell is assumed to meet the platinum loading target set by NETL 2012. As for SMR plant, constant annual improvement in energy efficiency is assumed, with the highest efficiency possible for current technology (DOE NETL 2001) representing the industry-wide average for 2030.

Table 5-1. Statistics for Technology Parameters

	ICEV20 FE	ICEV20P CO2 emission	BEV20 $LiMn_2O_4$ Specific energy	FCV20 Pt loading	FCEV20 FE
Unit	MPG	g/mile	Wh/kg	mg/cm2	MPG
Distribution	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal
Mean	44.5	182	178.89	0.3	60.89
Variance	79.21	1324.96	123.21	0.01	148.84

1. FE stands for fuel economy, and MPG stands for mile per gallon.
2. ICEV20 represents ICEV manufactured in 2020 and retires in 2030.
3. ICEV20P represents ICEV manufactured in 2020 which meets the national GHG emission standards on top of the CAFÉ standard.

Technology forecasting has its inherent uncertainty. Stochastic modeling is employed to address this uncertainty. For technologies for which historical performance metrics are available, mean and variance are calculated using the uncertainty propagation method described by McNerney *et al* 2011. For relatively new technologies, the predicted parameters are treated as the mean values, while the variances are determined to be square of 20 percent of the mean. Lognormal distribution is assumed for the parameters to be on the conservative side. Statistics of technology parameters for vehicles manufactured in 2020 are summarized in Table 5-1.

The environmental impacts are then evaluated in SimaPro 7.2 by Ecoindicator 99 (EI99) with the hierarchic perspective and average weighting in single score, Cumulative Energy Demand (CED) v 1.07and IPCC 2007 100-year Global Warming Potential (GWP) respectively.

5.3 Results

Life cycle impact results based on 1000 realizations of Monte Carlo simulation are presented in Figure 5-1, 5-2 and 5-3. For ICEV, no improvement in petroleum refining is assumed, so the reference case is identical to the case in which ICEV is manufactured in 2010 and retires in 2020. For BEV and FCV, the vehicle exclusive parts are the same for the reference case and the 2010 production case.

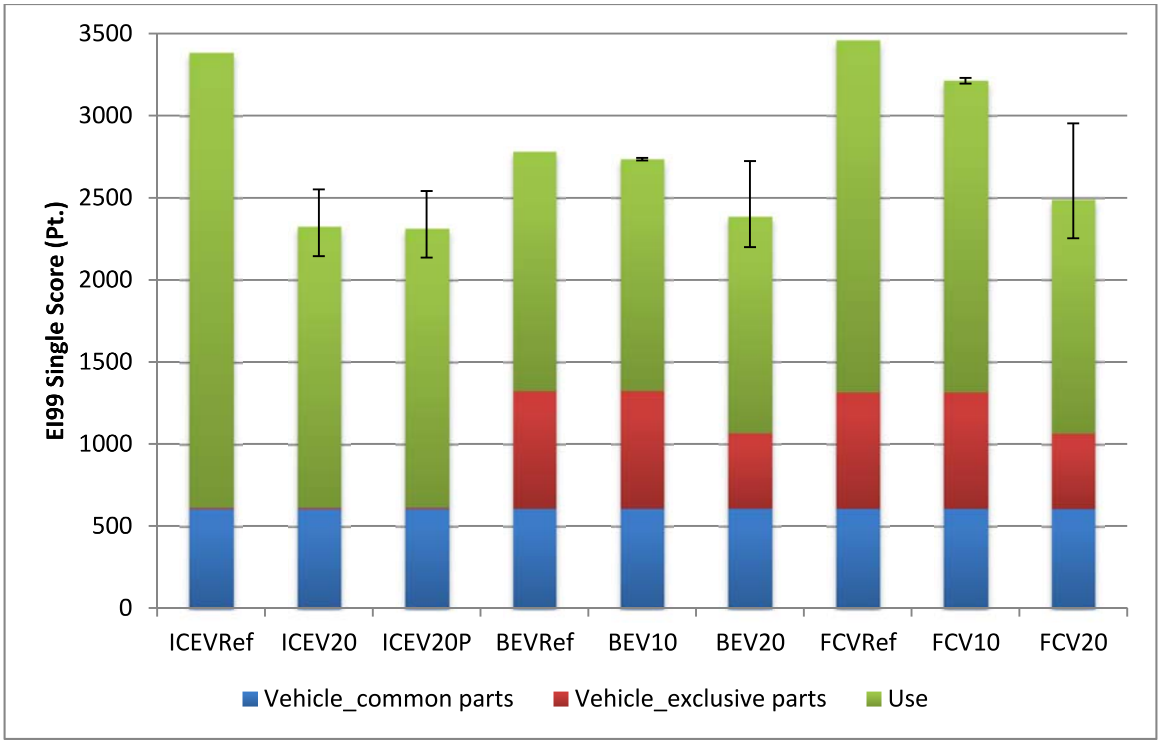

Figure 5-1. EI99 comparison of different passenger car LCA scenarios

1. Ref stands for reference case.
2. BEV10 stands for BEV manufactured in 2010 and retires in 2020.
3. The colored bars show the average of the Monte Carlo simulation. The error bars represent 95% confidence interval

For ICEV, complying with the new CAFÉ standard and national GHG emission standard could enhance the environmental performance by 30.9-49.7%. The environmental footprint of BEV can be reduced by 1.7-16.8% through continuous improvement in thermal efficiency of the NGCC power plant. The environmental impacts can be further mitigated by 14.3-26.0% via technological breakthrough in electrochemical properties of the lithium-ion battery. For FCV, increasing efficiency of the SMR plant alone results in a 7.1-11.7% reduction in its environmental burden. When coupled with future advance in fuel cell technology, up to a 25.0-28.0% cut in environmental scores is achievable.

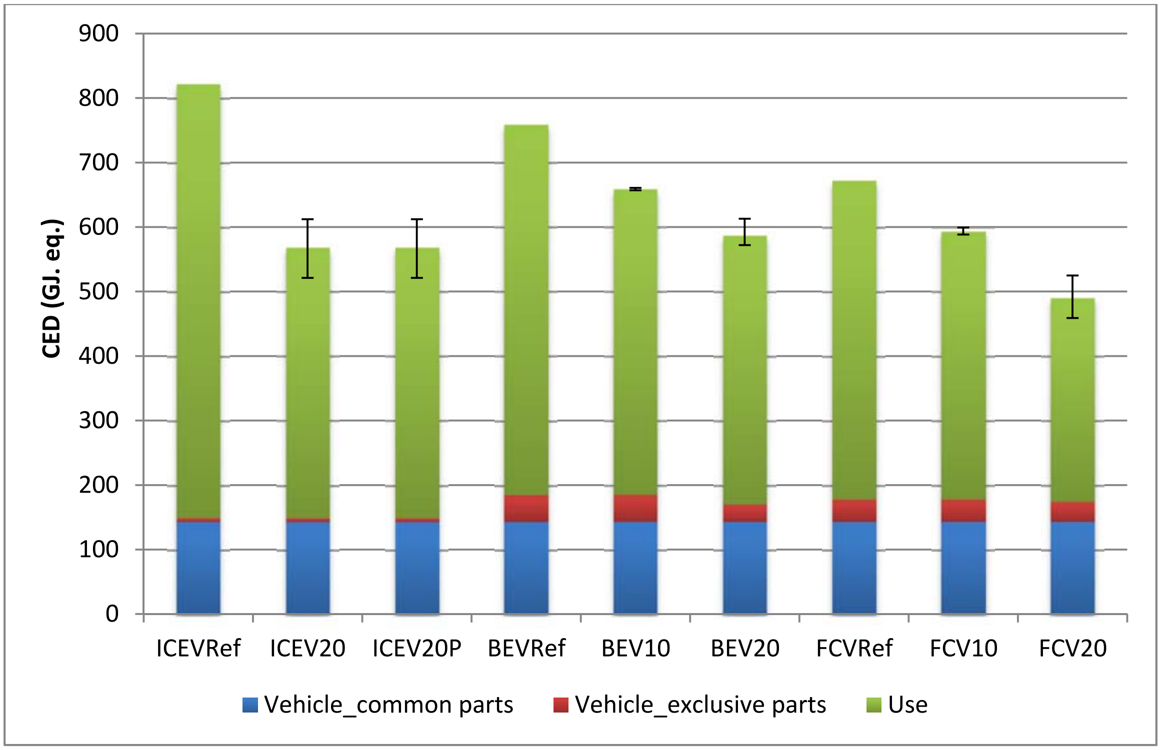

Figure 5-2. CED comparison of different passenger car LCA scenarios

5.4 Discussion

The results indicate that incorporating technological progression and future legislation has a significant impact on the outcome of LCA studies of passenger vehicles. The importance of legislation is mostly manifested in the case of ICEV, where no technology improvements are assumed for petroleum refinery or the vehicle itself, while the significance of technological advance can be observed in the case of BEV and FCV. A closer look at the impact of technological progression reveals that it largely depends on the maturity of a technology. LCA of technology at early diffusion stage is more likely to subject to this influence. For instance, a more rigorous environmental impact reduction is evident in the case of FCV compared with the case of BEV. By adopting technological progression model, we can quantify the pace of improvement for different technologies and use it as the basis for adjustment of time-series LCIs. This is especially useful in life cycle comparison of products with different room for technology development.

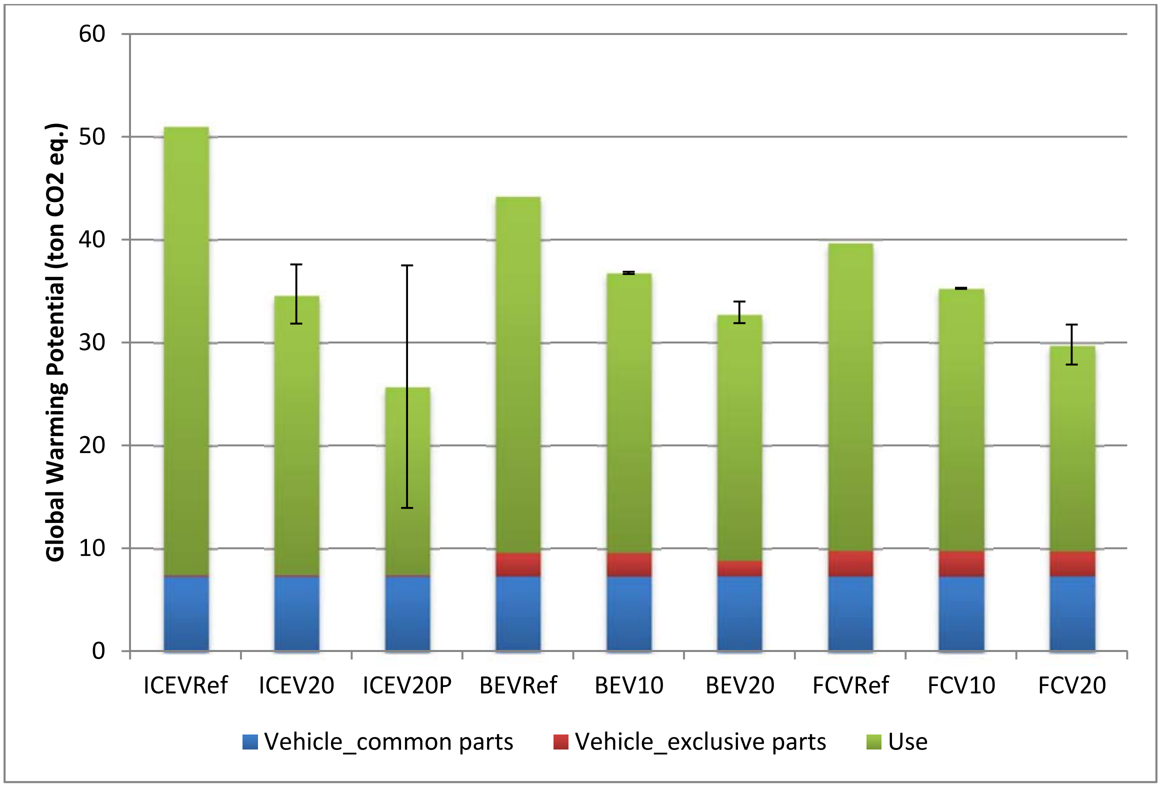

Figure 5-3. GWP comparison of different passenger car LCA scenarios

When considering technology evolution, improvement occurred once in a product's lifetime, such as making a better battery pack, and continuous improvement over the lifetime, such as ongoing transition to a greener grid, are of equal importance and should not be overlooked in LCA studies. The effect of one-time improvement is easier to detect, as the manufacturing phase environmental footprint is generally a linear function of the technology performance metric. Therefore, discounting of material or energy flows as employed in existing research is sufficient to account for such type of temporal variation. However, for continuous technological progression, due to its cumulative nature, a slight deviation in technology parameter could lead to substantial discrepancy in LCA results. For this reason, instead of throwing in a fixed discounting rate, the use technology prediction model is a better representation of the reality, and provides us with more confidence in LCA studies dealing with temporal variations.

It should be noted that by making time-adjusted changes to the LCI to tackle temporal variations, we are inevitably introducing additional uncertainty to the LCA study. For technologies with historical performance data, using technological forecasting model helps to reduce this uncertainty, as shown in the case of NGCC power plant. Even if historical performance data is not available, forcing Wright's law with literature value enables us to measure the uncertainty associated with our assumptions, as opposed to the constant discounting rate method, in which uncertainty is not quantifiable.

5.5 Conclusions

This paper presents a LCA study on three types of passenger vehicles in which technology progression model and future environmental policy are accounted for by a time-adjusted LCI as an attempt to address temporal variations. Comparing the environmental impacts of the technology-advancing case with the static reference case, it's concluded that the effect of technological improvement and legislation can be substantial in LCA, especially for long-lasting products at the innovation or early adoption stage. Incorporating technological forecasting model into LCA offers more insight into life cycle comparisons of fast-evolving technologies, as we are transitioning to a greener and low carbon economy.

References

Azevedo, L.B.; Henderson, A.D.; Van Zelm, R.; Jolliet, O.; Huijbregts, M.A.J. Assessing the importance of spatial variability versus model choices in life cycle assessment: the case of freshwater eutrophication in Europe. Environ. Sci. Technol. 2013, 47, 13565-13570.

Department of Energy, National Renewable Energy Laboratory 2001, Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming: http://www-pord.ucsd.edu/~sgille/mae124_s06/27637.pdf

Department of Transportation, National Highway Traffic Safety Administration 2012, 2017-2025 CAFÉ Final Rule: http://www.nhtsa.gov/staticfiles/rulemaking/pdf/cafe/2017-25_CAFE_Final_Rule.pdf

Dresen, B.; Jandewerth, M. Integration of spatial analyses into LCA – calculating GHG emissions with geoinformation systems. Int. J. Life Cycle Assess.2012, 19, 1094-1103.

Energy Information Administration 2013, Electric Power Annual 2012: http://www.eia.gov/electricity/annual/pdf/epa.pdf

EPA 2012, National Greenhouse Gas Emissions Standards for Model Years 2017-25: http://www.epa.gov/otaq/climate/documents/420f12051.pdf

Gasol, C.M.; Gabarrell, X.; Rigola, M. Gonzalez-Garcia, S.; Rieradevall, J. Environmental assessment: (LCA) and spatial modelling (GIS) of energy crop implementation on local scale. Biomass Bioenerg. 2011, 35, 2975-2985.

Haslam, G.E.; Jupesta, J.; Parayil, G. Assessing fuel cell vehicle innovation and the role of policy in Japan, Korea, and China. Int. J. Hydrogen Energ. 2012, 37, 14612-14623.

Idaho National Laboratory 2010, HTGR-Integrated Hydrogen Production via Steam Methane Reforming (SMR) Process Analysis; https://inlportal.inl.gov/portal/server.pt/document/78381/htgr-integrated_hydrogen_production_via_steam_methane_reforming_-smr-_economic_analysis_pdf

Kendall, A. Time-adjusted global warming potentials for LCA and carbon footprints. Int. J. Life Cycle Assess.2012, 17, 1042-1049.

Koh, H.; Magee, C. A functional approach for studying technological progress: extension to energy technology. Technol. Forecast. Soc. 2008, 75, 735-758.

Levasseur, A.; Lesage, P.; Margni, M.; Deschenes, L.; Samson, R. Considering time in LCA: dynamic LCA and its application to global warming impact assessment. Environ. Sci. Technol. 2010, 44, 3169-3174.

Leu, H.J.; Wu, C.C.; Lin, C.Y. Technology exploration and forecasting of biofuels and biohydrogen energy from patent analysis. Int. J. Hydrogen Energ. 2012, 15719-15725.

Majeau-Bettez, G.; Hawkins, T.R.; Stromman, A.H. Lief cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. Environ. Sci. Technol. 2011, 45, 4548-4554.

McNerney, J.; Farmer, J.D.; Redner, S.; Trancik, J.E. Role of design complexity in technology improvement. P. Natl. Acad. Sci. USA. 2011, 108, 9008-9013.

National Renewable Energy Laboratory 2012, National Fuel Cell Electric Vehicle Learning Demonstration Final Report:
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/learning_demo_final_report.pdf

Notter, D. A.; Gauch, M.; Widmer, R.; Wager, P.; Stamp, A.; Zah, R.; Althaus, H.-J. Contribution of Li-ion batteries to the environmental impact of electric vehicles. Environ. Sci. Technol. 2010, 44, 6550–6.

Performance Curve Database:
http://pcdb.santafe.edu/

Reap, J.; Roman, F.; Duncan, S.; Bras, B. A survey of unresolved problems in life cycle assessment. Part 1: goal and scope and inventory analysis. Int. J. Life Cycle Assess. 2008, 13, 290-230.

Reap, J.; Roman, F.; Duncan, S.; Bras, B. A survey of unresolved problems in life cycle assessment. Part 2: impact assessment and interpretation. Int. J. Life Cycle Assess. 2008, 13, 374-388.

Stasinopoulos, P.; Compston, P.; Newell, B.; Jones, H.M. A system dynamics approach in LCA to account for temporal effects – a consequential energy LCI of car body-in-whites. Int. J. Life Cycle Assess. 2012, 17, 199-207.

Tran, M.; Banister, D.; Bishop, J.D.K.; McCulloch, M.D. Realizing the electric-vehicle revolution. Nature Clim. Change. 2012, 2, 328-333.

Yuan, C.Y.; Simon, R.; Mady, N.; Dornfeld, D. Embedded temporal difference in life cycle assessment: case study on VW Golf A4 car. Proceedings of IEEE International Symposium on Sustainable Systems and Technology, Phoenix, AZ, May 18-20, 2009.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

With the increasing penetration of natural gas into the U.S. energy market, the environmental impacts associated with natural gas utilization in the transportation sector are worth investigating. This dissertation study is the first LCA study to systematically compare different passenger vehicles powered by natural gas. In this study, the environmental impacts of vehicle miles driven are evaluated for BEV, CNGV and FCV, each powered either directly or indirectly by natural gas.

Compared with conventional gasoline ICEVs, natural gas-powered passenger vehicles offer substantial environmental benefits by curtailing energy consumption, mitigating global warming and reducing emissions capable of damaging human health and ecosystem quality. Among the three mobility modes, CNGV appears appealing with regard to EI99 scores, because it does not possess power sources which add significant environment burden to the manufacturing stage of the vehicles, as in the case of BEV and FCV. However, CNGV is outperformed by BEV and FCV in the impact category of CED and GWP, due to lower overall energy conversion efficiency compared with the two.
For all the three transportation modes, the use phase dictates the life cycle environmental footprints, accounting for 63.5% - 81.9% of the total environmental scores. Therefore, improving energy conversion efficiency, both for well-to-tank, and for tank-to-well,

represents the biggest opportunity of environmental impacts reduction for the three vehicles.

For BEVs, the environmental performance is largely dependent on active cathode materials and their electrochemical properties. It's partly because that LIB accounts for up to 34.8% of the total life cycle impacts of BEV, and different active cathode materials have different material and energy demands in the synthesis process, which translated into different environmental burdens from the manufacturing phase. On the other hand, improvements in electrochemical properties of cathode material, for specific energy, cycle life or both, have the potential to reduce use phase impacts through battery light-weighting, increased battery efficiency and minimized battery pack requirement. For this reason, breakthrough in battery technology would also be the key to a more sustainable transportation by BEV.

If further technology advance were not possible, with current technology, LFP would be the most favorable cathode material for a BEV with respect to environmental friendliness, due to its superior cycling performance and lower energy and material requirement pertaining to the manufacturing of the cathode material. Sustainable production of LIB also provides windows of opportunity in environmental impacts reduction for BEVs, especially by cutting down active electrode materials and metal use, reducing process heat and organic solvent consumption, and recycling.

Besides battery technology development, switching to a greener electricity mix could also make BEV a more environmentally sound choice. Sensitivity analysis of BEV performance to electricity mix indicates that the outlook of BEV would be most optimistic for countries where electric grid is primarily powered by renewable sources. For the U.S., more electricity generation from natural gas also brings about additional environmental benefits from driving a BEV.

For FCV, the sole environmental hot spot is platinum use as catalyst at the electrodes, which represents 58.0-96.6% of the environmental footprint of the fuel cell. Reducing platinum loading is the single largest opportunity to ameliorate environmental damages entailed by manufacturing of the fuel cell. Recycling spent fuel cells is also an effective way to reduce environmental impacts from platinum extraction.

When it comes to infrastructure, adding a CCS unit to NGCC power plant or SMR plant has the potential to remarkably reduce GHG emissions, at the cost of moderately increased CED and EI99 score. Future CCS technologies with lower energy requirement for sorbents regeneration are in need if more rigorous GWP reduction targets are to be met without a considerable energy penalty.

This dissertation study is also the first to incorporate technological advances and environmental policy into LCA. BEV and FCV are under vigorous technology development. Combined with the long lifetime of vehicles, BEV and FCV are quite susceptible to temporal variations. In this study, Wright's law is applied to major technology performance metrics to make technological progression predictions; in addition, scenario analysis is carried out assuming CAFÉ standard and national GHG emission standard enforcement for ICEV, which together serve as the basis for time-adjusted LCIs of the three transportation options.

Based on a time-adjusted LCI, the environmental impacts of natural gas-powered vehicles can be decreased by up to 50%. This testifies the importance of including temporal variations in LCA study. With the ability to capture the actual trend of technology progression and account for uncertainty, it's evident that embedding technological forecasting model and environmental policy scenario analysis into LCA is a novel solution to the long-standing problem of temporal variation associated with traditional LCA.

To summarize, the dissertation study provides valuable insight into future environmental benefits and costs offered by natural gas-based personal passenger mobility alternatives that are commercially available. It would aid in a greener transition from coal and petroleum to natural gas, for the energy infrastructure and the transportation sector respectively.

6.2 Future Work

This dissertation study, however, has its own limitations and may need future improvements.

Firstly, conventional natural gas is assumed as the primary energy feedstock for this analysis, while future natural gas production would be more likely in the form of shale gas. The extraction of shale gas has invoked some controversy because it could impair the quality of groundwater and ecosystems in the vicinity of extraction wells. To better evaluate the environmental impacts by natural gas-powered mobility modes, especially to justify the environmental benefits of natural gas-based vehicles over conventional ICEVs for the coming decades, it would be desirable to replace current natural gas feed by a mix of conventional production and shale-gas production. This would necessitate LCA of shale gas production, which remains to be done as the environmental consequences resulted from shale gas extraction are still under investigation.

Secondly, the three transportation modes discussed in this dissertation doesn't exhaust possible future fleets that can be powered by natural gas. With current technology, another promising option of natural gas-powered transportation would be ICEV retrofitted to burn methanol derived from natural gas. Challenges associated with this pathway rest in the fuel conversion technology, as material and energy flow data for converting natural gas into methanol are nonexistent in current literature. More extensive literature review and data collection could make LCA of this pathway possible and thereby add width and depth to the presented study.

The dissertation study could be further improved in its methodology. To address temporal variation, this study only considered changes to time-series data on the LCI side. However, temporal variations could also exist on the life cycle impact assessment side, as pollutants emitted now should not exert the same environmental impacts as that emitted in the distant future. Nonetheless, to account for temporal variation in the realm of impact assessment, it requires knowledge on fate and transport modeling, as well as exposure and epidemiology analysis, and inevitably demands the collaboration of experts from a wide range of disciplines. The performance curve model employed in this study could shed some light on the new methodology development, suggesting that some quantitative linkage between time-series LCIs and corresponding environmental impacts need to be defined. The majority of the problem, unfortunately, remains to be an academic challenge.

Another limitation of the presented study is that possible interactions of the three transportation options are neglected. When modeling technological progression, we treated the three technologies as independent of each other. In reality, improvement in one technology could stimulate the technological development of competing technologies. Also, environmental legislation could also affect the trend of technological advance. To account for these interactions, economic input-out LCA and consequential LCA can be carried out for the three mobility modes.

In short, this study should be continually updated and improved as new technology parameters and LCA methodologies become available.