

# CHEMELECTROCHEM

## Supporting Information

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### **Paving the Way towards Highly Stable and Practical Electrolytes for Rechargeable Magnesium Batteries**

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## **Experimental details for sample preparation and instrumental analysis**

All sample handling and electrochemical testing was conducted in an argon filled MBraun glove box with O<sub>2</sub> and H<sub>2</sub>O content kept to less than 0.1 ppm. Magnesium borohydride (95%), sodium borohydride (90%), anhydrous tetrahydrofuran (THF), anhydrous 1,2-dimethoxyethane (DME), anhydrous dimethylsulfoxide (DMSO), and anhydrous acetonitrile (ACN) were purchased from Sigma Aldrich and used as received.

### **Sample preparation**

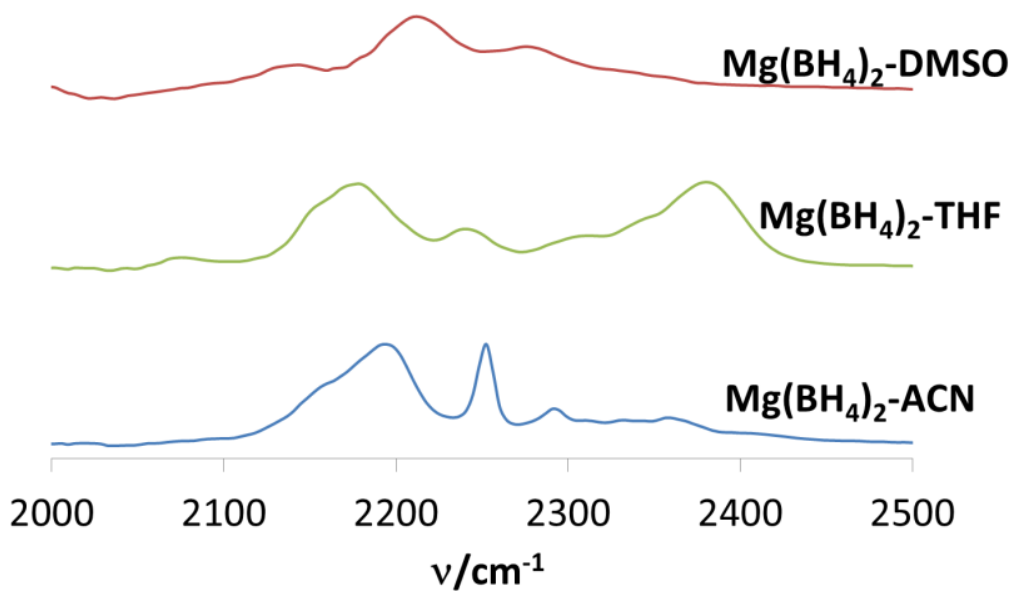
Mg(BH<sub>4</sub>)<sub>2</sub> or Mg(BH<sub>4</sub>)<sub>2</sub>/NaBH<sub>4</sub> were allowed to stir in the solvent of choice at room temperature for at least 2 hours. The solution was slightly hazy due to insoluble impurities present in the commercial borohydrides. A clear solution was obtained by filtration prior to use in all further experimentation.

### **Electrochemical testing**

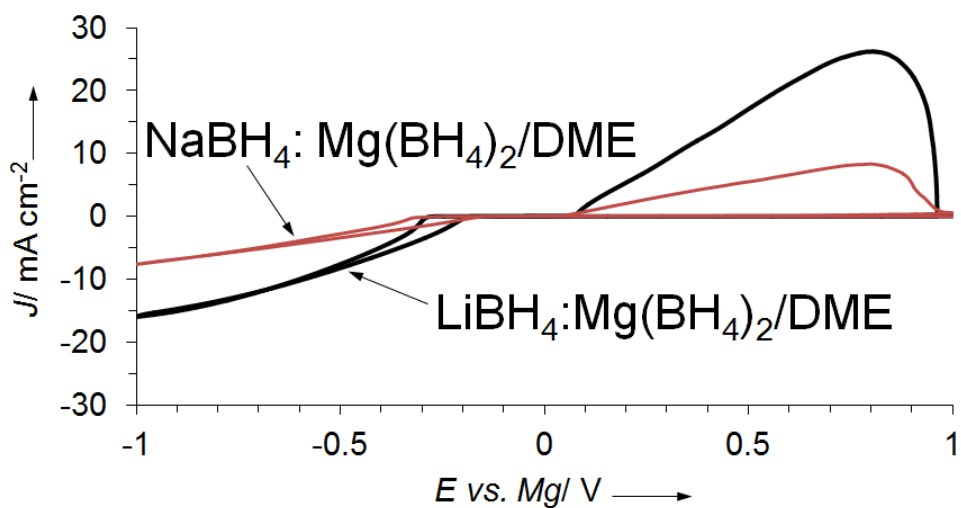
Using a Bio-Logic VMP3 multi-channel potentiostat, cyclic voltammetry experiments were conducted in a three electrodes BASi 4-dram shell vials using a 0.02 cm<sup>2</sup> Pt disk as the working electrode. All electrodes were polished, sonicated and kept in dry vacuum oven prior to each experiment. A magnesium wire and ribbon (BASi) were used as reference and counter electrodes, respectively. Oxides which may form on the surface of Mg electrodes during storage were removed prior to each experiment by rubbing their surface with a glass slide. Electrochemical testing was conducted using a Biologic potentiostat ran at a scan rate of 5 mV·s<sup>-1</sup>. The coulombic efficiency was calculated by dividing the oxidation charge over reduction charge. Conductivity measurements were conducted using a Pt electrode symmetrical cell. The cell constant was obtained by cell calibration using potassium chloride and was used to calculate to conductivity of the electrolyte

### **Infrared analysis**

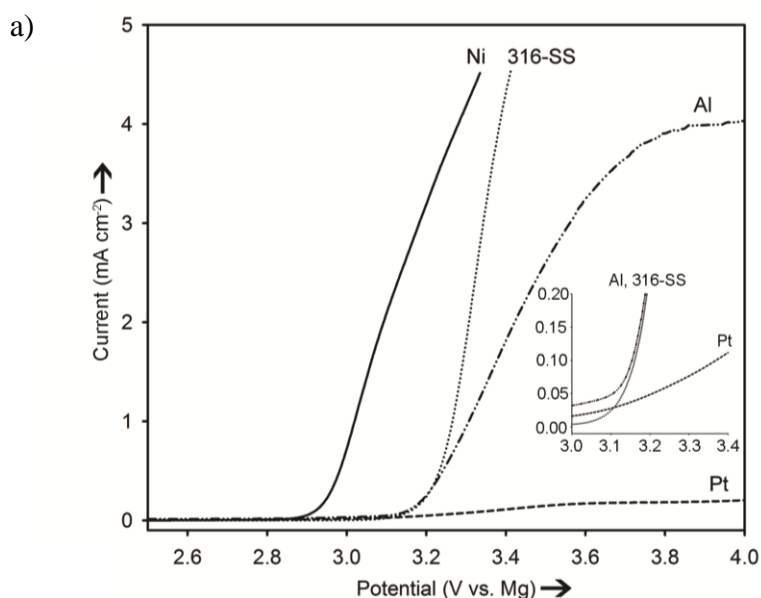
To prevent exposure to air during the analysis, an air tight Specac Smart Golden Gate ATR cell equipped with a diamond crystal was used in all IR analysis ran using a Nicolet 8700 FTIR (by Thermo Scientific).



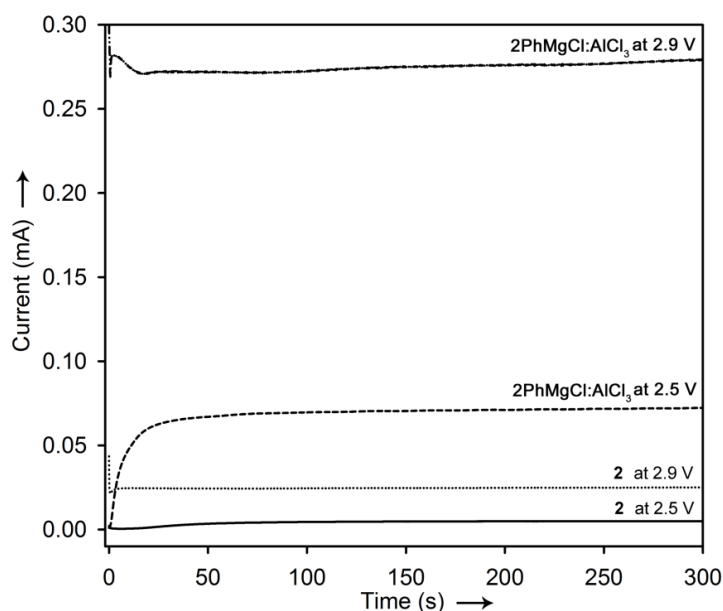
**Figure S1:** Comparison of the infrared spectra of  $\text{Mg}(\text{BH}_4)_2$  in THF, DMSO and ACN (chemical instability toward the borohydride was observed in the latter). The bands between  $2000\text{-}2500\text{ cm}^{-1}$  represent B-H stretching vibrations. The two strong widely separated vibrations ( $\text{Mg}(\text{BH}_4)_2/\text{THF}$ :  $2379\text{ cm}^{-1}$ ,  $2176\text{ cm}^{-1}$ ) were assigned to asymmetric  $\text{B-H}_t$  and  $\text{B-H}_b$  vibrations, respectively<sup>[1]</sup>. Discernable changes in the relative peak ratios of  $\nu\text{B-H}_t$  to  $\nu\text{B-H}_b$  and in their bands positions are reflective of enhanced salt dissociation.<sup>[1,2]</sup>



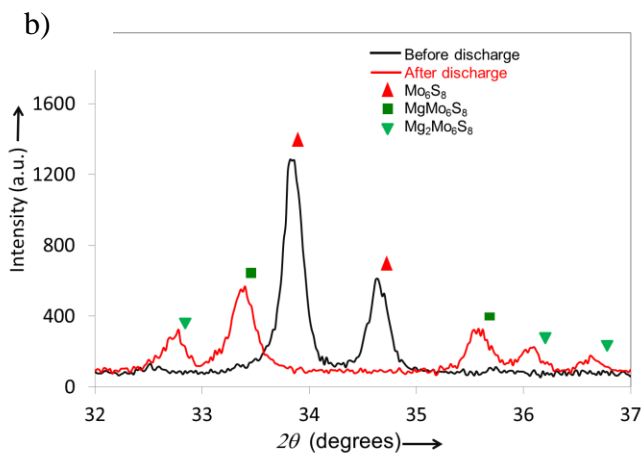
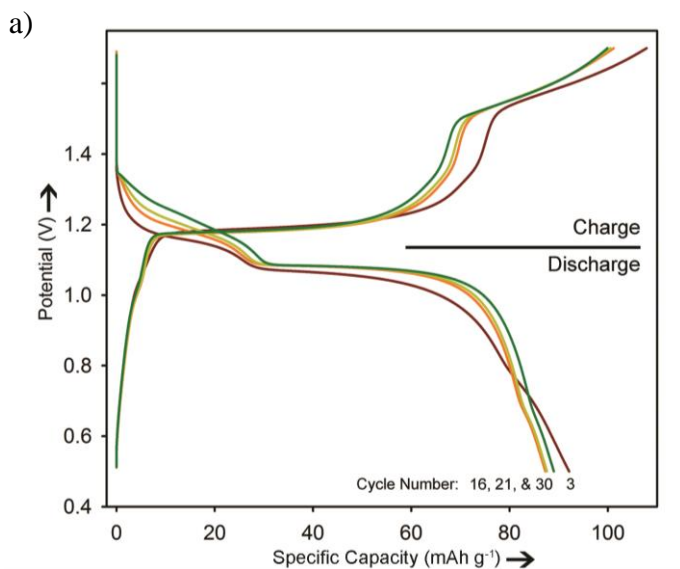
**Figure S2:** Cyclic voltammograms comparing Mg deposition/stripping for LiBH<sub>4</sub> (0.6 M): Mg(BH<sub>4</sub>)<sub>2</sub> (0.18 M) in DME and NaBH<sub>4</sub> (0.6 M): Mg(BH<sub>4</sub>)<sub>2</sub> (0.18 M) in DME electrolyte solutions.



b)



**Figure S3:** a) Linear scan voltammetry (LSV) of Mg(1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)Cl conducted on Pt, 316-SS, Ni and Al electrodes (Inset: Expanded view of oxidation onset) and b) Chronoamperometry on solutions of 2:1 PhMgCl:AlCl<sub>3</sub> and Mg(1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>)Cl (**2**) showing corrosion currents on 316-SS working electrodes at a variety of potentials. Adopted from reference 3 with permission. Copyright © 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure S4:** a) Typical charge/discharge profiles for a rechargeable battery with Mg(1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)Cl/THF as electrolyte, Mg anode and Chevrel phase cathode at cycle # 3, 16, 21, and 30, and b) XRD results of the cathode before/after discharge illustrating the characteristic peak shifts resulting from the magnesianation of Mo<sub>6</sub>S<sub>8</sub>. Adopted from reference 3 with permission. Copyright © 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

## References

- [1] R. Mohtadi, M. Matsui, T. S. Arthur, S.-J. Hwang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9780-9783; *Angew. Chem.* **2012**, *124*, 9918-9921.
- [2] M. Bremer, H. Nöth, M. Warchhold, *Eur. J. Inorg. Chem.* **2003**, *2003(1)*, 111.
- [3] T. J. Carter, R. Mohtadi, T. S. Arthur, F. Mizuno, R. Zhang, S. Shirai, J. W. Kampf, *Angew. Chem. Int. Ed.* **2014**, *53*, 3173-3177; *Angew. Chem.* **2014**, *126*, 3237-3241.