

POLYMER-MEMBRANE pH ELECTRODES AS INTERNAL ELEMENTS FOR POTENTIOMETRIC GAS-SENSING SYSTEMS

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SUMMARY

The use of polymer-membrane pH electrodes as internal sensing elements for the fabrication of inexpensive ammonia and carbon dioxide gas sensing systems is reported. The pH-responsive polymer membranes are prepared by incorporating tridodecylamine as the neutral carrier in plasticized poly(vinyl chloride) membranes. Both static and continuous-flow gas-sensing arrangements are described. For miniature static gas sensors, the internal polymer pH electrode can be made with or without an internal reference solution. In the latter case, the polymeric membrane is coated directly onto a graphite substrate. The polymer pH electrode can also be prepared in tubular form and used in conjunction with a gas dialysis chamber for automated continuous-flow determinations of carbon dioxide and ammonia. Slopes, response times, and reproducibility of these new gas-sensing systems are evaluated using optimized internal electrolytes, flow rates, and gas-permeable membrane materials. When appropriate reagents and materials are used, the static sensors exhibit slopes in the range 48–62 mV/decade with potentials reproducible to less than ± 1.5 mV at gas concentrations greater than 10^{-3} M.

The use of potentiometric gas sensors for the direct measurement of dissolved gases (NH_3 , CO_2 , NO_2 , etc.) or as final detectors for indirect bio-analytical methods involving enzymes and microbial cells has grown rapidly in recent years [1–3]. Commercial gas sensors commonly utilized in such applications have glass pH electrodes as internal elements [3]. Although these sensors often exhibit theoretically predicted response properties and Nernstian behavior [4], the commercial devices are rather large (tip diameter 12–15 mm) and expensive. Moreover, efforts to miniaturize these probes have been hampered by the fragile nature of the glass electrode and the flat bottom geometry required for functional static gas sensor designs.

In view of the limitations imposed by the use of glass electrodes, several workers have prepared gas sensors with alternative internal pH-responsive transducers. Mascini and Cremisini [5] reported the use of thermo-molded antimony-type pH electrodes as inner elements while workers at General Electric have patented the concept of using electrodes based on palladium or iridium oxide for the fabrication of miniature CO_2 sensors [6]. Unfortunately, metal/metal oxide pH transducers may be subject to interferences from the redox environment of the sample (e.g., oxygen content) and this could limit their utility in the design of stable gas sensing systems.

Over the past few years, our research efforts have focused on replacing the traditional glass-membrane electrodes in gas sensors with polymer-membrane ion-selective electrodes [7-11]. Thus far, polymer membranes responsive to ammonium and carbonate ions have been utilized, along with appropriate internal buffer reagents, to prepare small, inexpensive, and rugged gas sensors for NH_3 and CO_2 [7-9]. The polymer-membrane electrodes have also been fabricated in a novel tubular form and used in conjunction with a gas dialysis chamber and flowing internal electrolyte to develop attractive automated continuous-flow gas sensing arrangements [11, 12].

Recently, Schulthess et al. [13] introduced a new pH-responsive polymer membrane electrode based on the incorporation of tridodecylamine in a poly(vinyl chloride) (PVC) matrix. Although the use of this polymer pH membrane has already been suggested for the fabrication of inexpensive gas sensors [8], it is the purpose of this paper thoroughly to evaluate and document this approach. Miniature static as well as automated CO_2 gas-sensing arrangements are described and evaluated. The feasibility of utilizing polymer-coated graphite pH electrodes within the miniature static probes is also examined. It will be shown that when constructed with appropriate internal electrolytes, gas-permeable membranes, etc., the resulting gas-sensing devices have response properties that compare favorably with the costly commercial glass pH electrode-based probes.

EXPERIMENTAL

Apparatus and materials

All potentiometric measurements were made using a Corning model 12, a Fisher Accumet model 620, or an Altex SelectIon 2000 pH/mV meter, and were recorded on either a Heath/Schlumberger model SR-204 or a Houston Instruments Omniscrite strip-chart recorder. Potentials for the polymer-membrane pH electrodes were evaluated against a saturated calomel reference electrode (SCE).

A schematic diagram for the automated CO_2 -sensing system is shown in Fig. 1. The ammonia system was essentially the same, except that the segmented stream required debubbling prior to passage through the dialysis chamber. The dialysis block and mixing coils were heated to 30°C for CO_2 determinations. Two dialysis chambers were used for these studies, one with a channel/volume ratio of 1:1, and the other with a volume ratio of 1:4. These chambers were fitted with a polytetrafluoroethylene (PTFE) membrane (W. L. Gore Inc.) for the NH_3 -sensing system and a silicone polycarbonate membrane (General Electric) for the CO_2 -sensing system.

Reagents

All chemicals used were of reagent grade. Standard solutions and buffers were prepared with distilled, deionized water.

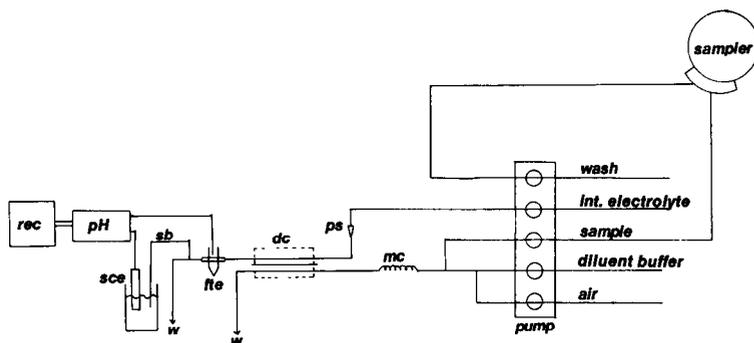


Fig. 1. Schematic diagram of automated carbon dioxide assay system: (rec) recorder; (pH) pH-mV meter; (SCE) saturated calomel reference electrode; (sb) salt bridge; (fte) flow-through electrode; (w) waste; (dc) dialysis chamber; (ps) pulse suppressor; (mc) 7-turn mixing coil.

The pH-sensitive polymer membrane consisted of tridodecylamine, sodium tetraphenylborate (Eastman Kodak), poly(vinyl chloride) (chromatographic grade; Polysciences), and dibutyl sebacate (Sigma Chemical Co.).

In the automated system for carbon dioxide, the flowing internal electrolyte was a 0.001 M NaHCO_3 solution prepared in 0.01 M NaCl. The diluent stream was 0.1 M citrate buffer (pH 4.45). Various concentrations of sodium hydrogencarbonate were prepared as standards for calibration purposes. The internal reference solution for the tubular electrode was 0.5 M citrate buffer (pH 4.45) containing 0.1 M NaCl.

For the automated ammonia-sensing system, the flowing internal electrolyte was 0.001 M NH_4Cl . The diluent was 0.001 M NaOH. Several concentrations of ammonium chloride were prepared as standards for calibration purposes. The internal reference solution for the polymer pH electrode was 0.01 M NH_4Cl .

Preparation of polymer pH electrodes and gas sensors

Polymer pH electrodes were of two types, those with and those without internal reference solutions. Preparation of the polymer pH membrane and its incorporation into pH electrodes with internal reference solutions were described previously [8]. A schematic diagram of a pH electrode without the internal reference solution and the corresponding static gas sensor is shown in Fig. 2. This electrode consists of a 0.5-mm diameter graphite rod (Pentel Hi-Polymer mechanical pencil lead) encased in a stainless steel syringe needle for strength and to provide electrical contact. This assembly is encased in heat-shrink tubing to provide insulation. The tip of the graphite rod is left exposed and is fitted with a piece of PVC tubing to provide a suitable surface for bonding the membrane. The pH-sensitive membrane is applied dropwise (as a solution in tetrahydrofuran) to the tip. The gas sensors were constructed from pipet tips as described earlier [7]. The gas-

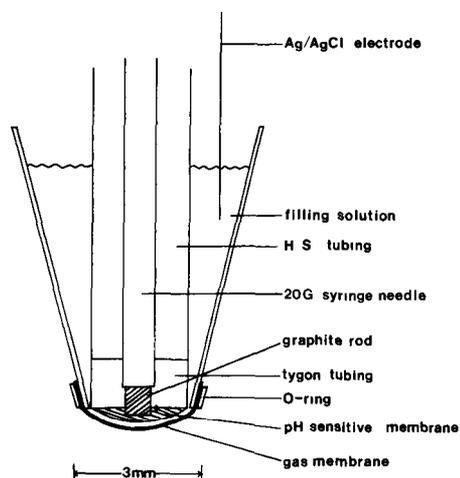


Fig. 2. Schematic diagram of static gas-sensing system utilizing a coated-graphite pH electrode.

permeable membrane used was microporous PTFE ($0.2\text{-}\mu\text{m}$ pore; W. L. Gore and Assoc.). The tubular flow-through pH electrodes were prepared as described previously for ammonium and carbonate systems [9, 11].

These electrodes and corresponding gas sensors were evaluated for potentiometric response and analytical utility under the specific conditions described below.

Calibration curves for pH electrodes and static sensors

Potentiometric response for the polymer-based pH electrodes was obtained in a solution which was 0.05 M each in sodium acetate, tris-[hydroxymethyl]-aminomethane hydrochloride, and *N*-[2-acetamido]-2-aminomethanesulfonic acid. Microliter volumes of sodium hydroxide or hydrochloric acid were added to this solution and the actual pH was monitored after each addition with a calibrated glass pH electrode (Fisher 13-639-90). The potential of the polymer-membrane electrode (vs. SCE) was plotted vs. the measured pH value. Results for the static CO_2 gas sensors were obtained from additions of sodium hydrogencarbonate to a 0.1 M citrate buffer (pH 4.5) while data for the ammonia sensors were obtained from additions of ammonium chloride to 0.1 M NaOH. Measurements were usually made at room temperature.

RESULTS AND DISCUSSION

Static pH electrodes

Conventional polymer-based pH electrodes are those that have internal reference solutions. Their performance has been described [4, 13] and the response characteristics of our electrodes are essentially the same. There is,

however, a possible problem when attempts are made to use conventional polymer pH electrodes (i.e., ones with internal reference solutions) in gas-sensing configurations. Analyte gas dissolved in the thin electrolyte film of the sensor may diffuse through the PVC ion-selective membrane and change the pH of the internal reference solution. This would result in errant or drifting response. Indeed, this behavior has been exploited to produce a hydrogen carbonate ion-selective electrode [14], which in reality functions as an inverted gas sensor. Thus, in order to produce useful gas sensors, the internal reference solution of the pH electrode must be buffered. Four buffers were evaluated to establish which would best maintain a constant pH in the internal reference solution. The buffers investigated were 0.1 M and 1 M phosphate-HCl, pH 7.0, and 0.1 M and 1 M citrate-HCl, pH 4.2. For this study, an Orion 95-02 gas-sensor body was used with a pH-sensitive polymer membrane as the gas-permeable membrane and the various buffers as the internal filling solutions. The pH of the thin buffer film was monitored with the internal glass pH electrode as the analyte gas (NH_3 or CO_2) concentration was increased. Although all of the buffers worked well, the 1 M citrate buffer yielded best results, holding the pH change to just 0.03 units even for gas concentrations as high as 10^{-2} M. Because it was found later that the 0.5 M and 0.25 M citrate buffers worked nearly as well, these were used for all subsequent experiments to prevent large osmotic effects.

Coated-substrate pH electrodes were also evaluated. Both graphite rods and platinum wires were used as substrates. For most experiments, graphite electrodes were used because it was easier to make them with the proper flat-bottom geometry desirable for good gas-sensor design and response. A calibration curve for the coated graphite pH electrode is shown in Fig. 3. The electrode responds logarithmically (typical slopes of 59–64 mV/10-fold change in H^+ activity) to changes in hydrogen ion activity between pH 4 and 10. Response was observed as low as pH 2 and as high as pH 12. Response times to reach equilibrium potentials were typically 15–20 s per unit pH change. Equilibrium was assumed when the potential drift was less than 0.4 mV min^{-1} . Depending on the electrode, the reproducibility of potentials on consecutive calibrations can be as good as $\pm 1 \text{ mV}$ or as poor as $\pm 4 \text{ mV}$. Day-to-day reproducibility with regard to absolute potential values was found to be poor, although the slopes remained relatively constant. One possible explanation for this has to do with the nature of the inner reference potential of the coated substrate electrodes. This inner potential system is usually described as a metal/metal oxide half-cell with the necessary oxygen coming from diffusion of oxygen and water through the polymer membrane [15]. Changes in the oxygen concentration of the surrounding electrolyte will change the oxygen concentration in the membrane and perhaps alter the metal-oxide layer on the inner conductor. This will produce drifting or unstable potentials. Keeping the membrane hydrated apparently slows this process and helps to improve the reproducibility somewhat. In general, it was found that the coated-graphite pH electrodes were more stable than the coated-wire types.

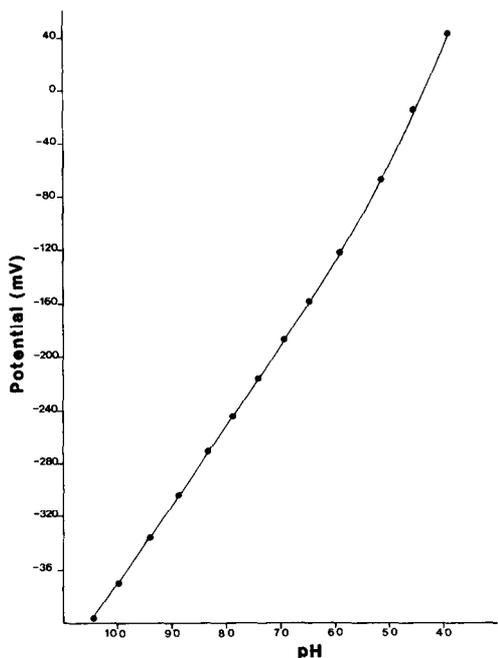


Fig. 3. Typical calibration curve for the coated-graphite pH electrode.

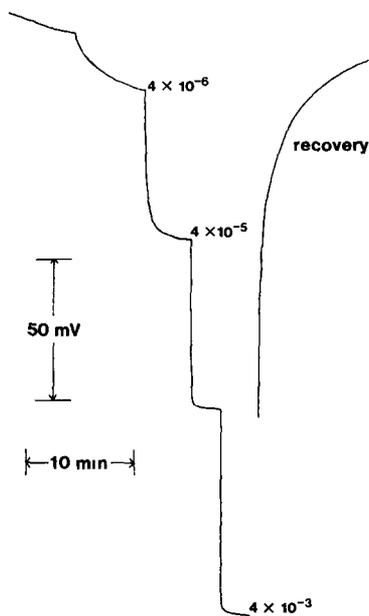


Fig. 4. Typical chart recording showing response and recovery times for the static ammonia sensor. Molar concentrations are given on the curves.

Static gas sensors

Gas sensors were constructed from both conventional polymer pH electrodes and coated-graphite electrodes. Both types of sensors displayed similar response properties. To avoid repetition, the response characteristics of the conventional polymer pH electrode-based sensors will be discussed in detail and only significant differences between the two will be mentioned.

An important parameter controlling gas-sensor response is the composition of the internal filling solution. The components of this solution and their concentrations determine the detection limits, slope, and time response of the sensor [4]. In order to obtain optimal response with the ammonia sensor, four internal filling solutions were evaluated. Two were commercial solutions (Orion 95-10-02 and HNU 10-10-01) and two were laboratory preparations (0.01 M NH_4Cl in 0.1 M NaCl and 0.1 M NH_4Cl). The laboratory preparations performed better than the commercial ones, giving slopes that were typically 57–60 mV/decade. The 0.1 M NH_4Cl solution gave the best dynamic measurement range, but the solution which was 0.01 M NH_4Cl in 0.1 M NaCl yielded lower detection limits and faster response times. The results described below were obtained using the latter solution.

The static ammonia gas sensor was evaluated for time response, linear response range, slope, and reproducibility. Figure 4 shows a typical recording

for the NH_3 sensor response as ammonium chloride was added to a 0.1 M NaOH solution. The time response was slow at low concentrations (5–10 min) but improved rapidly with increasing gas concentration. It can also be seen that the recovery time of the sensor, when placed into a fresh solution of sodium hydroxide without ammonia, was similar to that of commercial ammonia sensors (i.e., 20 min). A typical calibration curve for the ammonia gas sensor is shown in Fig. 5. Near-Nernstian response (59–62 mV/decade) was observed from 2×10^{-5} M to 4×10^{-2} M ammonia. The detection limit was estimated to be of the order of $1\text{--}2 \times 10^{-6}$ M. With regard to reproducibility, seven consecutive calibrations on a given day, yielded a slope of 61.2 ± 0.8 mV over a range from 4×10^{-5} M to 4×10^{-2} M ammonia. However, variations in the absolute potentials at equal analyte concentrations were somewhat greater, ranging from ± 2.5 mV at a concentration of 4×10^{-5} M to ± 1.6 mV at 4×10^{-3} M. Day-to-day reproducibility of absolute potentials was poor, because of evaporation of the internal filling solution. For best results, the internal filling solution should be renewed daily, and as with any membrane electrode system, the sensor should be calibrated before and after measurements of unknowns.

The CO_2 gas sensor was evaluated in a similar fashion. Again, four filling solutions were studied: HNU ISE 10-22-02, Orion 95-02-02, 0.01 M NaHCO_3 in 0.1 M NaCl, and 0.01 M NaHCO_3 in 0.25 M NaCl. The last solution was evaluated in an attempt to establish whether matching the osmolarity of the internal filling solution with that of the sample solution would reduce e.m.f. drift caused by diffusion of water vapor. Drift was reduced, but the performance of both of the laboratory-prepared solutions was inferior to that obtained with the commercial solutions. Operation with the commercial

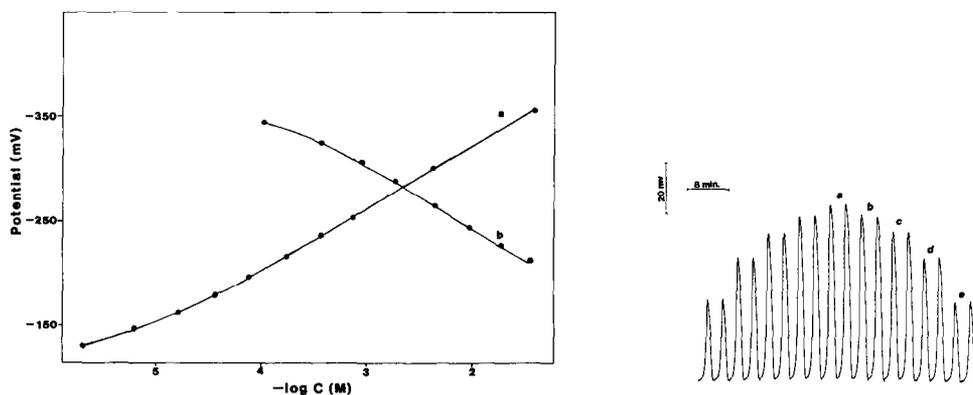


Fig. 5. Typical calibration curve for the static sensors based on an internal polymer membrane pH electrode: (a) ammonia; (b) carbon dioxide.

Fig. 6. Typical strip-chart recording obtained for automated CO_2 system. Concentrations refer to NaHCO_3 standards placed into the sampler: (a) 1×10^{-3} M; (b) 8×10^{-4} M; (c) 6×10^{-4} M; (d) 4×10^{-4} M; (e) 2×10^{-4} M.

solutions yielded larger linear response ranges and improved slopes. The HNU internal filling solution was used for all subsequent experiments.

Another important parameter of the CO₂ gas sensor is the selection of the gas-permeable membrane. Silicone rubber membranes are often used in commercial CO₂ sensors rather than PTFE membranes. However, in the particular sensor configuration evaluated in this work, difficulties in attaching the silicone rubber membranes severely limited their usefulness; such membranes did not fit the shape of the sensor well and tended to leak. Thus, the PTFE membrane was used exclusively in the fabrication of the static gas sensors.

Response times for the static CO₂ sensor ranged from 7 min at concentrations of 10⁻⁴–10⁻³ M to less than 1 min at concentrations greater than 10⁻³ M. Figure 5 shows a typical calibration curve for the polymer pH electrode-based CO₂ sensor. Response is logarithmic (slopes of 48–53 mV/decade) from 2 × 10⁻⁴ M to 4 × 10⁻² M CO₂. Reproducibility is generally the same as for the ammonia gas sensor (±2.5 mV at low gas concentrations, ±1.5 mV for concentrations greater than 10⁻³ M).

In general, the static sensors prepared with the polymer membrane pH electrodes possess response properties quite similar to those of conventional glass pH electrode-based probes. The one major difference is the larger variation in absolute potentials from day to day. However, provided that appropriate calibration procedures are used, the new devices appear to perform adequately.

Automated systems

The automated NH₃- and CO₂-sensing systems described here utilize the same chemical detection principles as the static sensors described above. The configurations used to adapt the static sensors to the automated mode are variations of those described previously [11] based on a tubular ammonium ion-sensitive polymer membrane electrode as the detector. These variations along with response characteristics for each system are presented below.

Of the two systems constructed, the CO₂ sensing system was the more extensively studied. In developing this system, the aim was to optimize the operating parameters to permit low-level CO₂ measurements with good sample throughput. The continuous flow manifold shown in Fig. 1 differs in several ways from that described earlier [11]. A major change in the apparatus involved utilizing the sample stream without removing the air segmentation. A microporous teflon membrane was used in the gas dialysis chamber for the ammonia system [11]. Air can pass through that membrane resulting in large open circuit noise in the detection stream. Therefore, for the CO₂ system, a homogeneous silicone polycarbonate membrane was used, through which air bubbles do not permeate. The advantage of using an air-segmented sample stream is that it allows for more of the sample CO₂ to be detected. This is because any CO₂ formed in the sample slug will equilibrate with the adjacent air bubbles. Removal of these air bubbles results in

a substantial loss of the total CO_2 sample. Using this arrangement, the signal resulting from low CO_2 concentrations was greatly increased.

As Durst [16] has suggested, the sensitivity of the system can be enhanced by increasing the flow rate of the sample stream relative to the recipient stream. To this end, a flow rate ratio of 2:1 was used. This results in a concentration effect of the sample in the recipient electrolyte stream because this stream is flowing much more slowly than the sample stream. In an effort to improve further the sensitivity of the system, a special dialysis chamber was prepared with the recipient stream being 1/4 the volume of the sample stream. If the system was allowed to reach equilibrium using this chamber, with solutions of equal pH in both streams, the concentration of sample in the recipient stream would be 80% of that originally present in the sample stream relative to only 50% for the usual channel ratio of 1:1. Therefore, although equilibrium is never actually achieved and the two streams do not actually have the same pH value, in practice, using the 1:4 chamber enables the recipient stream to contain a higher concentration of sample and thus results in a larger signal.

The concentration of the electrolyte in the recipient stream also plays an important role in the sensitivity of the system. Bailey and Riley [17] reported that the concentration of the electrolyte should be ten times higher than the lowest sample concentration to be quantified. This is because low levels of CO_2 cannot produce a large enough pH change to be detected when the electrolyte is too concentrated. Several concentrations of electrolytes were examined and 10^{-3} M NaHCO_3 was found to be the best for samples containing between 10^{-4} M and 10^{-3} M CO_2 . Figure 6 shows a typical strip-chart recording for the CO_2 detector based on the tubular polymer membrane pH electrode, operating at 20 samples per hour. It can be seen that the automated system displays excellent precision with peak potentials generally reproducible to ± 1 mV. Resulting calibration graphs typically had slopes of 53–58 mV/decade with a logarithmic range from 2×10^{-4} to 10^{-3} M CO_2 . For determinations of carbon dioxide at levels above 10^{-3} M, higher concentrations of sodium hydrogencarbonate in the recipient stream are recommended.

The ammonia-sensing system was constructed similarly to that described earlier [11] except that the ammonium ion-selective membrane used in the tubular electrode was replaced with a pH-sensitive one. Good results were obtained with this system, but it was not as sensitive as the one utilizing the ammonium ion-selective electrode. That system had lower detection limits because it utilized a "buffer trap" effect (i.e., the recipient stream is buffered to an appropriate pH so that NH_3 is converted to NH_4^+ , thus preventing any loss of analyte by diffusion). Obviously this could not be done in gas-sensing systems based on pH detection. Although measuring pH changes does not provide a system optimized for the determination of low levels of ammonia, it does offer a convenient method of determining higher concentrations over a larger concentration range.

In summary, several designs for static and automated ammonia and carbon dioxide gas sensors based on polymer pH-sensitive membrane electrodes have been evaluated. In view of their low cost, simple design, and ease of miniaturization, these gas sensors offer an attractive alternative to gas-sensing devices based on conventional glass pH electrodes.

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