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Nonaqueous Mg Flow Battery with a Polymer Catholyte

Yunan Qin,‖ Kathryn Holguin,‖ Dillon Fehlau, Chao Luo,* and Tao Gao*

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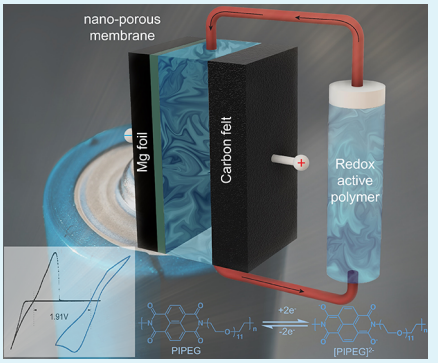
ABSTRACT: Redox flow batteries (RFBs) are promising for the large-scale storage of renewable energies. Nonaqueous RFBs can achieve higher voltages and are more suitable for extreme environments than their aqueous counterparts. In this work, the first nonaqueous Mg flow battery with a polymer catholyte is reported, by integrating a Mg foil anode, and a porous membrane, with a polymer solution catholyte. The battery can deliver a voltage of 1.74 V, a capacity of 250 mAh/L, and a cycle life of 50 cycles. This work demonstrates the feasibility of Mg flow batteries and provides a unique direction for flow battery research.



KEYWORDS: *flow battery, magnesium anode, nonaqueous electrolyte, polymer, porous membrane*

Redox flow batteries (RFBs) are promising technologies for large-scale stationary energy storage.[1,2] RFBs with nonaqueous electrolytes have the potential to achieve higher voltages and to be operated at more extreme temperatures than their aqueous counterparts due to the wide electrochemical stability window of organic solvents.[3] However, this potential has not been fully exploited due to a lack of stable anode materials with low redox potentials.[4,5] Among various anode materials for nonaqueous RFBs, Mg metal stands out as a promising anode because of its low redox potential (−2.4 V vs SHE), high capacity (3833 mAh/cm^3), abundance, and low cost.[6] Nonetheless, flow batteries based on Mg chemistry are barely reported despite the remarkable progress that has been made to advance the performance of Mg-ion batteries.[7,8] In this work, the first nonaqueous Mg flow battery with a polymer catholyte is demonstrated.

The realization of a nonaqueous Mg flow battery is largely impeded by a lack of conductive ion-exchange membrane in nonaqueous electrolytes, especially in ethereal electrolytes.[9] The flow battery reported here addresses this challenge by integrating a porous membrane with a polymer solution catholyte (Figure 1a). The chemical structure of the polymer is shown in Figure 1b and confirmed by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) (Figure S2−6). The molecular weight of the PIPEG polymer was measured by gel permeation chromatography (GPC). Its number-average molecular weight (M_n) is 7.3 kg mol^{-1}, and the dispersity (M_w/M_n) is 2.1. Overall, the polymer (PIPEG) bears a naphthalenetetracarboxylic dianhydride (NTCDA) moiety as the redox-active center for the electrochemical redox reaction during battery charging/discharging (Figure 1c). The carbonyl groups in the NTCDA moieties reversibly gain and lose two electrons, providing a redox plateau at ∼1.91 V vs Mg/Mg^{2+} (Figure 3a). A polyethylene glycol (PEG) moiety is designed into the polymeric structure to enhance its solubility in the ether-based electrolyte due to the similar polarity of polyether to that of the dimethoxyethane (DME) solvent, and a maximum solubility of 4 g/L can be achieved. The nanopores of the porous membrane allow ions to pass through it freely while blocking the polymer molecules to some extent due to their large polymeric backbone structure.

Cyclic voltammetry (CV) measurement of the PIPEG catholyte was performed at different scan rates (Figure 2a). The relationship between peak current and $v^{1/2}$ was plotted (Figure 2b) and linearly fitted, and the diffusion coefficient D_0 of PIPEG was calculated to 3.0 × 10^{-9} cm^2/s based on the Randles−Sevcik equation,[10] which is lower than those of small organic molecules (typically ∼10^{-6} cm^2/s)[11−13] due to the large size of the polymer but comparable to those of other polymer molecules of similar molecular weight.[13] The natural log of the peak reduction current (i_{pa}) scales linearly with the difference between the voltage at the peak reduction current (E_{pa}) and the calculated E_0 of the reduction reaction (Figure 2c), and the heterogeneous reduction rate constant k^0 of PIPEG was 1.4 × 10^{-4} cm/s from the slope of a linear fitting of

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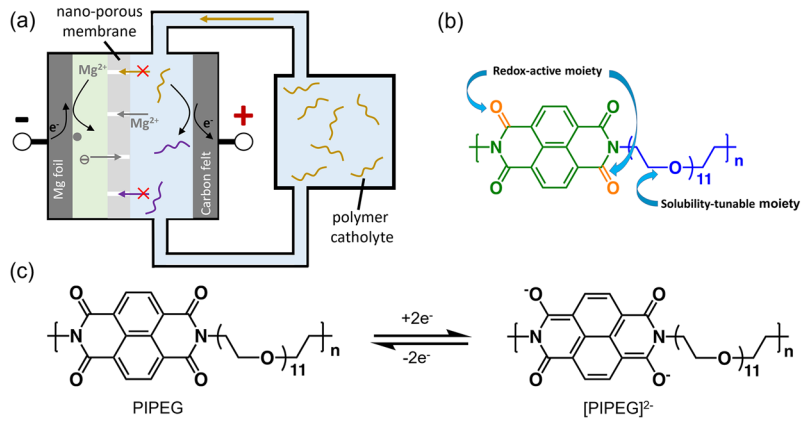

Figure 1. (a) Schematic of the Mg/polymer flow battery. The flow battery is made with a Mg foil anode, a porous membrane, and a polymer solution catholyte. (b) The structure of the polymer. (c) The reaction mechanism of the polymer during battery discharge/charge.

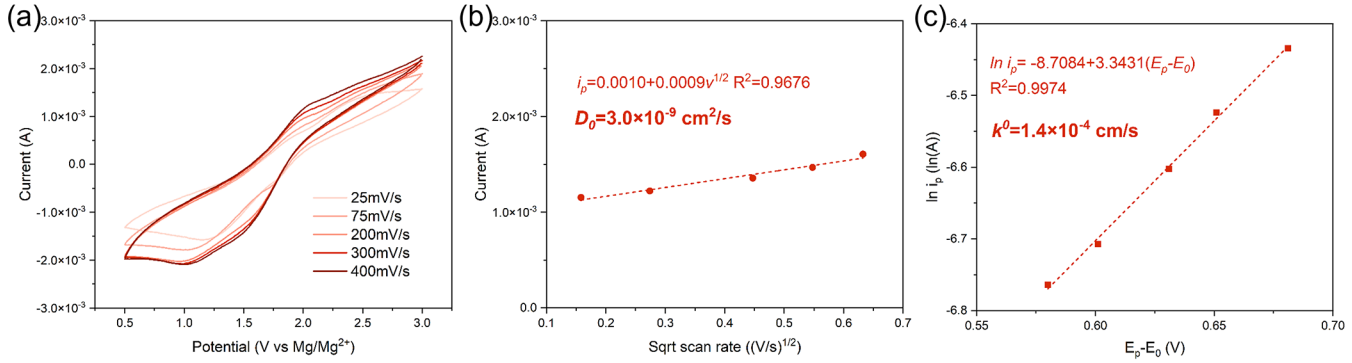

Figure 2. (a) Cyclic voltammograms of the 4g/L PIPEG catholyte obtained at different scan rates. (b) Relationship between peak current and $v^{1/2}$ of the cyclic voltammograms of the PIPEG catholyte. (c) For the 4g/L PIPEG catholyte, the linear fit of the natural log of peak reduction current (i_{pa}) versus the difference between the voltage at the peak reduction current (E_{pa}) and the calculated E_0 of the reduction reaction.

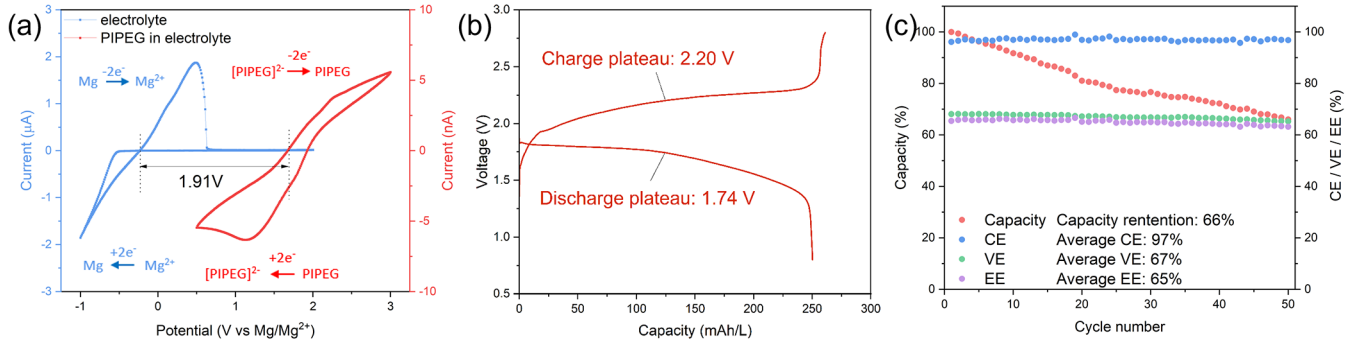

Figure 3. Electrochemical performance: (a) CV of the Mg anode and polymer catholyte, (b) discharge/charge curve of the battery, and (c) cycling performance of the battery.

the curve based on the previously reported method.[10] This reaction rate constant is higher than that of Fe^{3+}/Fe^{2+} in aqueous electrolytes,[14,15] suggesting the fast reaction kinetics of the polymer catholyte.

The redox potentials of the Mg anode and polymer cathode are illustrated in Figure 3a, which shows the battery can provide a voltage of 1.91 V when there is no kinetic loss. The electrochemical performance of the nonaqueous Mg flow batteries was measured by a lab-made flow cell (Figure S1). A typical voltage curve of the flow battery is given in Figure 3b, which shows a discharge plateau centered at 1.74 V and a charge plateau centered at 2.20 V. At a catholyte concentration of 4 g/L, the battery can deliver a volumetric capacity of 250 mAh/L at 50 μA/cm^2, corresponding to an energy density of 0.44 Wh/L. The capacity retention, Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) during cycling are shown in Figure 3c. The battery retains 66% of the initial capacity at the 50th cycle. The average CE, VE, and EE are 97%, 67%, and 65%, respectively.

The nonunity CE suggests there is still some crossover of the polymer molecules during battery cycling. The nonunity VE and EE can be attributed to the ohmic loss and kinetic loss of the cathode and anode reactions.[16] The capacity loss during cycling can be attributed to three possible causes. First, the

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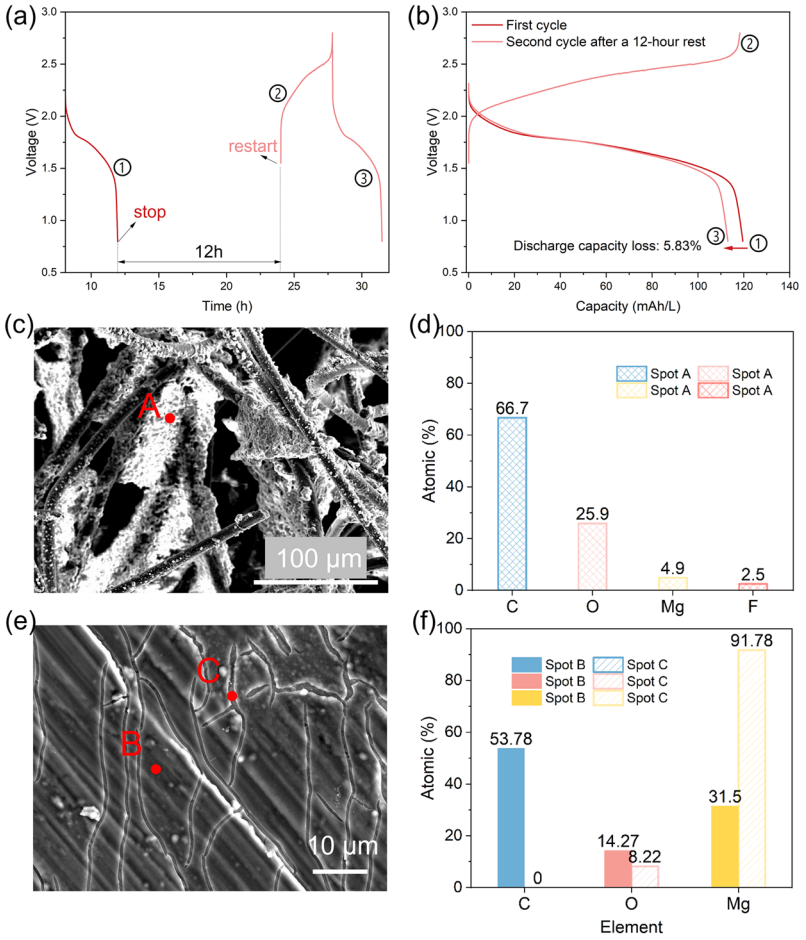

Figure 4. (a) Voltage−time profile of two consecutive cycles separated by a 12 h rest. Catholyte concentration: 2 g/L. (b) Voltage−capacity profile of two consecutive cycles. (c) SEM image and (d) EDS analysis of the washed carbon felt recovered from the cycled flow cell cathode. (e) SEM image and (f) EDS analysis of the washed Mg ribbon recovered from the cycled flow cell anode.

volume of the catholyte solution decreased by 20% after 142 h cycling. Since no obvious leakage from the cell was observed during the experiment, the reduced catholyte volume could result from the evaporation of DME solvent and the subsequent active material precipitation. Second, the discharged state of PIPEG is unstable, which is revealed in the following test. The cell was discharged to 0.8 V first and then put into rest. After the 12 h rest, the test was resumed. The discharge capacities before and after the rest are compared (Figure 4a,b). The result shows that the cell loses 5.83% of the capacity after resting at the discharged state, which is much higher than the typical capacity loss per cycle during a normal cycling without a long rest (0.68%). The scanning electron microscopy (SEM) image (Figure 4c) of the recovered carbon felt from the cycled flow cell shows the presence of some solid particles, and energy dispersive spectroscopy (EDS) (Figure 4d) shows this solid contains large amounts of C and O, suggesting the discharged molecules precipitated from the solution due to an irreversible chemical reaction. Lastly, PIPEG permeated through the membrane and underwent an irreversible reaction with the Mg foil anode. The permeability of PIPEG (in DME) through the porous membrane is measured to be 8.20% per day, indicating the polymer could still pass through the membrane despite its large size. An SEM image (Figure 4e) of the Mg foil anode recovered from cycled flow cells shows a film covering its surface. EDS (Figure 4f) shows it contains C, O, and Mg elements, suggesting that the cross-overed polymer reacted with the Mg anode.

To improve the cycling performance of the nonaqueous Mg flow batteries, several approaches can be implemented in future studies. Electrolytes based on organic solvents with lower vapor pressure can mitigate the evaporation of solvent during battery cycling. A porous membrane with smaller pores and a polymer with large molecular size can further suppress the crossover. In addition, polymers that are stable at its reduced state and not reactive with Mg can be developed to inhibit undesirable side reactions during battery cycling. To enhance the energy density of the Mg flow battery, the following strategies can be considered. Since the repeating unit of the redox-active polymer in this work consists of two moieties, a redox-active moiety and a solubility-tunable moiety, the redox-active moiety (NTCDA) can be modified to increase its redox potential, while the solubility-tunable moiety (PEG) can be tailored to enhance the solubility in the ethereal electrolyte. For the former, electron-withdrawing functional groups, such as a cyano group, nitro group, etc., can be introduced into the NTCDA moiety. In addition, anion insertion-based redox-active moieties, such as the nitroxide free radical or triphenylamine, can be used as alternatives to the NTCDA moiety due to their higher redox potential. For the latter, the number of ether groups in the PEG moiety can be tuned to adjust the polarity of the polymer. A systematic study

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to reveal the correlation between the number of ether groups in the PEG moiety and the solubility in the ether-based electrolyte is necessary to identify the PEG moiety with the highest solubility. Additionally, the dependence of polymer solubility on its molecular weight needs to be understood to balance solubility and permeability. To enhance the power performance, Mg anode reaction kinetics can be improved by using porous Mg electrodes or tuning the electrolyte composition.

In conclusion, a novel flow battery based on a Mg anode, a porous membrane, and a polymer solution catholyte is demonstrated in this work, which validates the feasibility of nonaqueous flow batteries based on the Mg redox chemistry and opens a unique direction for energy storage technology research. The problems of the Mg flow battery and potential strategies to overcome them for enhancing the flow battery performance are discussed, which provide guidelines for future research. The results reported here can serve as the benchmark for future studies on Mg flow batteries. Given the high capacity and low redox potential of the Mg anode and the wide voltage window of the nonaqueous electrolyte, a high-voltage (3 V), high-capacity (13.4 Ah/L), and high-energy-density (40 Wh/L) flow battery can be obtained if a cathode material with high redox potential and high solubility (0.5 M) can be identified. These efforts are undertaken in our laboratories, and the results will be reported in future publications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.2c00363.

Experimental details and discussion for material characterization (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Tao Gao − *Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112-9057, United States;* orcid.org/0000-0003-0204-3269; Email: taogao@chemeng.utah.edu

Chao Luo − *Department of Chemistry and Biochemistry and Quantum Science & Engineering Center, George Mason University, Fairfax, Virginia 22030, United States;* orcid.org/0000-0001-8497-8548; Email: cluo@gmu.edu

Authors

Yunan Qin − *Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112-9057, United States*

Kathryn Holguin − *Department of Chemistry and Biochemistry, George Mason University, Fairfax, Virginia 22030, United States*

Dillon Fehlau − *Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112-9057, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.2c00363

Author Contributions

‖Y.Q. and K.H. contributed equally.

Notes

The authors declare no competing financial interest.

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