Study of the Electrochemical Behavior of High Voltage Vanadium-Metal Hydride Hybrid Semi-Flow Battery

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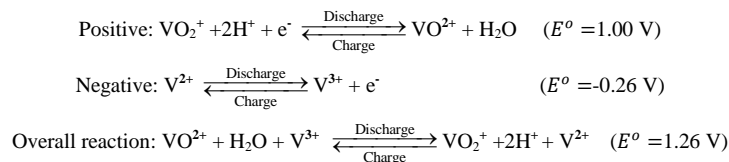† * Corresponding Author Tel: +(852) 2859 7917, Fax: +(852) 2857 1586,
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A vanadium-MH rechargeable semi-flow battery hybridizing the V^{4+}/V^{5+} redox couple (positive) with the metal hydride (negative) was investigated to increase the cell voltage greatly and eliminate the problems of V^{2+} oxidation. The experimental open circuit voltage of 1.86 V and operating voltage of 1.65 V for this hybrid battery were obtained, very high values among all rechargeable flow batteries. The system demonstrated superior stability, reversibility, and efficiencies in coulomb (97%), energy (81.3%), and voltage (83.8%).

Introduction

Flow batteries [1-4] are actively studied for storing electricity, particularly intermittently generated from solar, wind, and other renewable sources [5]. The all-vanadium redox flow (VRF) battery [6, 7] is one of the most promising flow batteries, but still requiring improvements and development [8].

Theoretical specific energy of VRF battery is 60.5 Wh/kg. The VRF battery (as shown in Scheme 1) is acidic and has a positive V^{4+}/V^{5+} electrolyte at a standard potential of 1.0 V coupled with a negative electrolyte V^{2+}/V^{3+} at -0.26 V, giving a theoretical cell voltage of 1.26 V.

$$\text{Positive: } VO_2^+ + 2H^+ + e^- \xrightleftharpoons[\text{Charge}]{\text{Discharge}} VO^{2+} + H_2O \quad (E^o = 1.00 \text{ V})$$

$$\text{Negative: } V^{2+} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} V^{3+} + e^- \quad\quad (E^o = -0.26 \text{ V})$$

$$\text{Overall reaction: } VO^{2+} + H_2O + V^{3+} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} VO_2^+ + 2H^+ + V^{2+} \quad (E^o = 1.26 \text{ V})$$
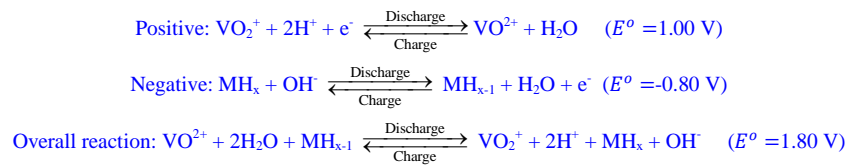
Scheme 1. Electrochemistry of VRF.

Serious attempts were made to improve vanadium flow battery technology by alternative pairing of negative and positive electrode/electrolyte reactions into a hybrid cell [9-14]. Skyllas-Kazacos et al. [9] reported a hybrid Vanadium-O_2 redox fuel cell, thus eliminating the mass of the positive side as oxygen can be freely stored in air. The reported specific energy is > 40 Wh/kg, about 1.6 times the practical specific energy of conventional VRF battery, whereas the reported open circuit voltage (OCV) was kept in

the range of 1.10 to 1.24 V. But the oxygen reaction is highly irreversible and the absence of a good bi-functional electrocatalyst leads to low voltage efficiency. A vanadium chloride/polyhalide redox flow battery proposed by the same group [14] increased the specific energy significantly as a consequence of higher vanadium concentration can be used in the presence of mixed electrolyte, and with an experimental OCV of 1.3 V. Crossover of ions through the membrane was reduced during operation. Both attempts give similar OCV to that of the conventional VRF battery.

With the concept of pH differential between an alkaline negative electrode and acidic positive electrode, higher cell voltages have been demonstrated for H_2-O_2 fuel cells [15-17] and PbO_2/$PbSO_4$-MH_x/MH_{x-1} rechargeable batteries [17-20]. A bipolar membrane was used to provide the ionic contact as well as barrier in the pH differential cells [16, 17, 19, 20]. The lead acid/MH system reported a stable operating voltage with repeated charge/discharge cycles at 2.6 V (30% and 86% increase from individual lead-acid and NiMH batteries). The higher voltage and increased capacity is a result of the extra energy store/released in acid-alkaline neutralization corresponding to ΔG^o=-79.85 kJ/mol [17, 18].

It is conceptually attractive to increase the voltage of vanadium flow battery with introduction of a pH differential by coupling the positive V^{4+}/V^{5+} with a negative alkaline electrode/electrolyte. Moreover, the problem of V^{2+} oxidation can be eliminated. In this paper, we combine the advantages of the vanadium redox flow battery and the acid/alkaline hybrid battery, and demonstrate a novel semi-flow vanadium-metal hydride (V-MH) hybrid rechargeable battery. Additional neutralization energy can be stored in the electrolyte and liquid flow minimizes fouling and enhances the function of the ionic interfaces. In principle, this hybrid battery system of V^{4+}/V^{5+} and metal hydride can deliver an overall cell capacity of 111 mAh/g, cell voltage of 1.8 V, and specific energy of 200 Wh/kg, much higher than that of conventional VRF battery. This paper reports the electrochemical properties of the new hybrid flow battery, cell voltage, electrode overpotentials, and voltage across membrane are monitored during idle, charge and discharge. The electrochemistry of this V-MH flow battery is shown in Scheme 2.

$$\text{Positive: } VO_2^+ + 2H^+ + e^- \xrightleftharpoons[\text{Charge}]{\text{Discharge}} VO^{2+} + H_2O \quad (E^o = 1.00 \text{ V})$$

$$\text{Negative: } MH_x + OH^- \xrightleftharpoons[\text{Charge}]{\text{Discharge}} MH_{x-1} + H_2O + e^- \quad (E^o = -0.80 \text{ V})$$

$$\text{Overall reaction: } VO^{2+} + 2H_2O + MH_{x-1} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} VO_2^+ + 2H^+ + MH_x + OH^- \quad (E^o = 1.80 \text{ V})$$
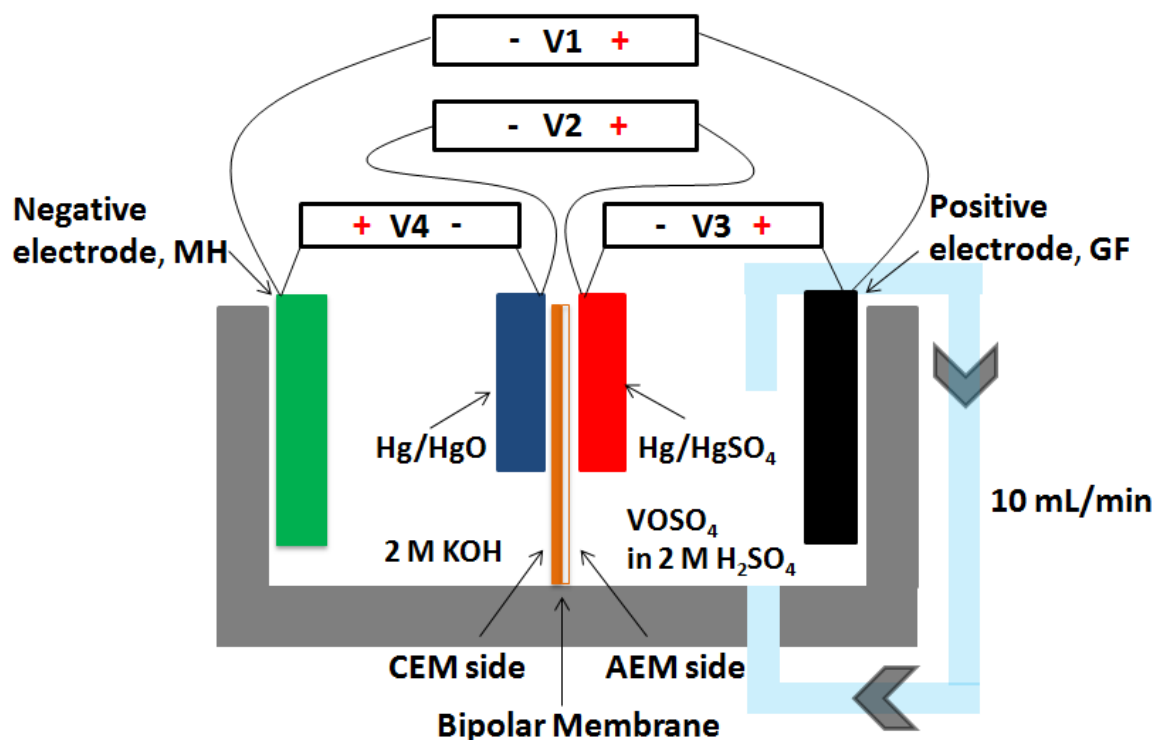
Scheme 2. Electrochemistry of V-MH.

Fig. 1. Schematic drawing of the V-MH hybrid system with positive electrolyte flow. V1: Potential difference between GF electrode and MH_x/MH_{x-1} electrode or overall cell potential. $V1 = \phi_{positive} - \phi_{negative}$; V2: Potential across bipolar membrane or potential difference between reference electrodes Hg/Hg_2SO_4 and Hg/HgO. $V2 = \phi_{Hg/Hg2SO4} - \phi_{Hg/HgO}$ (Here the reference electrode Hg/HgO in alkaline solution is arbitrarily defined as reference electrode as it is immersed into the negative chamber); V3: Potential difference between graphite felt (GF) electrode (positive electrode) and reference electrode (Hg/Hg_2SO_4). $V3 = \phi_{positive} - \phi_{Hg/Hg2SO4}$; V4: Potential difference between MH_x/MH_{x-1} electrode (negative electrode) and reference electrode (Hg/HgO). $V4 = \phi_{negative} - \phi_{Hg/HgO}$.

Experimental and Results

Electrode preparation

Commercial graphite felt (Shenhe Carbon Fiber Materials Co. Ltd., Liaoning, China) was used as positive electrode and had an active surface area of around 9 cm^2 with a thickness of 5 mm, these graphite felt were pre-treated before use. The pre-treatment as follows: the graphite felt (GF) was soaked in 95% (wt%) H_2SO_4 at 50 ^{o}C for 2 h. Rinsed it with DI water until the effluent pH is near neutral and then heat treated at 60 ^{o}C for 2 h to improve its electrochemical activity and hydrophilicity. The negative MH_x electrode was prepared by 1 g of $LaNi_5$ based metal-hydride alloy powder extracted from a commercial GP-2700 AA battery. The $LaNi_5$ based powder was mixed with 50 mg XC-

72 vulcan carbon (4.5 wt%), pasted and pressed on nickel foam. The active area of MH_x electrode was around 9 cm^2.

The initial 0.064 mol/L positive $VOSO_4$ electrolyte was prepared from dissolving 0.274 g $VOSO_4 \cdot nH_2O$ (Dieckmann Chemical Industrial Co. Ltd., Hong Kong, n=2.85 according to thermogravimetric analysis) in 20 mL 2 mol/L H_2SO_4 solution, respectively.

<u>Vanadium-MH flow battery design</u>

The hybrid battery had two compartments (See Fig. 1). The acid chamber contained a graphite felt positive electrode immersed in 0.064 mol/L positive $VOSO_4$ electrolyte in 2 mol/L H_2SO_4 solution, while the alkaline chamber contained a MH_x negative plate inserted in 20 mL 2 mol/L KOH aqueous solution. The two chambers were separated by a bipolar membrane (Membrane International Inc., USA). The active area of the bipolar membrane is 20 cm^2 with a dimension of 40 mm (L) x 50 mm (H). The membrane was preconditioned by immersing into 5 wt% NaCl solution over night before use. The volume of each acid and alkaline electrolyte was about 20 mL in a chamber of dimensions 46 mm (L) $\times$68 mm (H) $\times$ 10 mm (W). The flow rate was fixed at 10 mL/min for the $VOSO_4$ electrolyte in the positive chamber of Vanadium-MH system.

<u>Electrochemical tests and cell performance</u>

All electrochemical performance tests were carried out at room temperature. Galvanostatic charge and discharge measurements were carried out with Voltalab PGZ301. $Hg/HgSO_4$ (filling solution: 2 mol/L H_2SO_4) and Hg/HgO (filling solution: 2 mol/L KOH) are employed as reference electrodes in the acid and alkaline chambers of the Vanadium-MH system, respectively. The positive electrolyte was circulated in the positive chamber through Phar-Med NSF-51 tube by using Watson-Marlow Bredel's 323 peristaltic pump at 10 mL/min. The hybrid system was left idle for 1 hour, and then charge and discharge at constant current of 9 mA (1 mA/cm^2) in all runs. The cut-off voltage is 2.0 V - 1.6 V. During idle and operation, the overall cell potential (V1), the potential across the membrane (V2), and the electrode potential versus corresponding reference electrode: $Hg/HgSO_4$ (V3) and Hg/HgO (V4) were recorded by National Instrument PCI-6221 Data Acquisition (as shown in Fig. 1).

Performance of individual components of the V-MH cell can be evaluated from the four voltage profiles V1-V4, as shown in Fig. 2 for 5 charge and discharge cycles. For the overall cell voltage, V1, the charge and discharge plateaus are stable throughout the 5 cycles at c.a. 1.86 V, and 1.65 V, respectively.

As shown in Fig. 2, the shape of the charge/discharge curves (V1) resembles that of the positive electrodes (V3), whilst the voltage loss between charge and discharge of the MH negative electrode (V4) remains small. The present setup of V-MH is therefore limited by the positive side. Throughout the cycles, the voltage loss across the membrane

(V2) remains stable at 0.4 to 0.6 V, indicating a steady and reversible process of ionic transport.
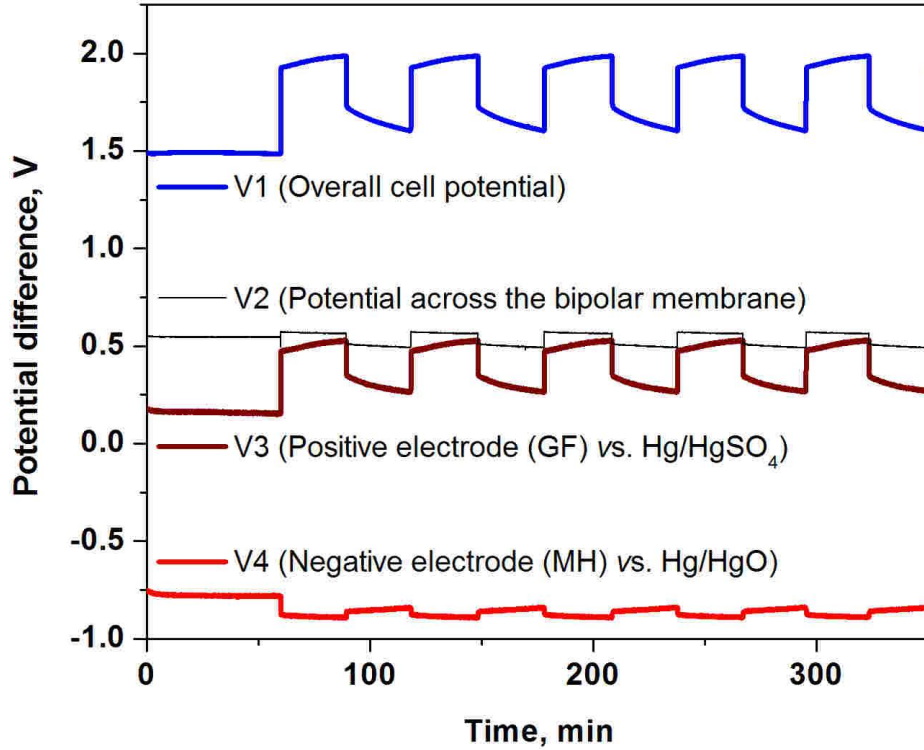

Fig. 2. 5 charge and discharge cycles (1st-5th) of V-MH battery. V1: Potential difference between GF electrode and MH_x/MH_{x-1} electrode or overall cell potential. V1=$\phi_{positive}$ - $\phi_{negative}$; V2: Potential across bipolar membrane or potential difference between reference electrodes Hg/Hg_2SO_4 and Hg/HgO. V2= $\phi_{Hg/Hg2SO4}$ - $\phi_{Hg/HgO}$ (Here the reference electrode Hg/HgO in alkaline solution is arbitrarily defined as reference electrode as it is immersed into the negative chamber); V3: Potential difference between graphite felt (GF) electrode (positive electrode) and reference electrode (Hg/Hg_2SO_4). V3= $\phi_{positive}$ - $\phi_{Hg/Hg2SO4}$; V4: Potential difference between MH_x/MH_{x-1} electrode (negative electrode) and reference electrode (Hg/HgO). V4= $\phi_{negative}$ - $\phi_{Hg/HgO}$.

Efficiencies of the V-MH battery are analysed from the voltage profiles. In the first cycle, the overall cell voltage V1 takes around 29.4 minutes to reach 2.00 V. Then it discharges with a plateau of 1.65 V for c.a. 29 minutes until the 1.6V cut-off, with a charge efficiency of 98.6%. In the 5th cycle, the charge efficiency maintained with an operating voltage ~1.65 V. As shown in the matching V1 and V3 curves, which indicates the positive side mainly determines the overall cell performance in this case.

Voltage efficiency, defined as (averaged discharge voltage)/(averaged charge voltage), is 83.8% at the end of the 5th cycle. Corresponding energy efficiency is 81.3%. These

values are much higher than those of the VRF battery, as shown in Table 1. One disadvantage of VRF battery over other conventional batteries is its low specific energy. With this semi-flow V-MH battery, the theoretical specific energy can be increased up to 200 Wh/kg, 3.5 times that of VRF battery. In addition to a higher discharge voltage, the efficiency in voltage, coulombic, and energy for V-MH battery improved. Specifically, the voltage efficiency is 83.8% compared to 62-73% for VRF, while the charge efficiency was maintained at 97%. Higher energy efficiency 81.3% was obtained for V-MH battery, compared to 66-75% for VRF, representing an increase of >8%.

Table 1. Comparison of V-MH and VRF batteries in terms of average voltage, coulomb, and energy efficiencies.

Battery type	Nominal voltage, V	Voltage efficiency[b], %	Coulombic efficiency[c], %	Energy efficiency[d], %
V-MH	1.65	83.8	97	81.3
VRF[8]	1.25	62-73	80-98	66-75

[b] Voltage efficiency: $\eta_V = V_{discharge}/V_{charge}$
[c] Coulomb/charge efficiency: $\eta_c = Q_{discharge}/Q_{charge} = (It_{discharge})/(It_{charge})$
[d] Energy efficiency: $\eta_P = E_{discharge}/E_{charge} = (V_{discharge}It_{discharge})/(V_{charge}It_{charge})$

Improvement over the preliminary results of the lab-scale V-MH system are expected with optimization in electrolyte flow rates, concentrations, electrodes material, membrane thickness, or other cell and operation parameters. The power and specific energy of the V-MH hybrid battery can be further increased with scale-up. Depends on the application, the hybrid system can provide further specific improvement over existing options of VRF, lead acid, or MH systems.

Conclusions

A novel semi-flow Vanadium-Metal Hydride (V-MH) system (200 Wh kg^{-1}) with 3.5 times higher theoretical specific energy than that of the conventional all vanadium redox flow battery (60.5 Wh kg^{-1}) was reported. Hybridizing the V^{4+}/V^{5+} couple with metal hydride eliminates the problem of V^{2+} oxidation as in VRF battery. The average voltage of the Vanadium-MH battery system during discharge is around 1.65 V, which is higher than that of individual all vanadium redox flow battery (1.2 − 1.4 V) and NiMH$_x$ battery (1.25 − 1.35 V). The Vanadium-MH battery system has good reversibility and efficiency in voltage (83.8%), coulombic (97%) and energy (81.3%), which is critical for its potential application.

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Figure Captions

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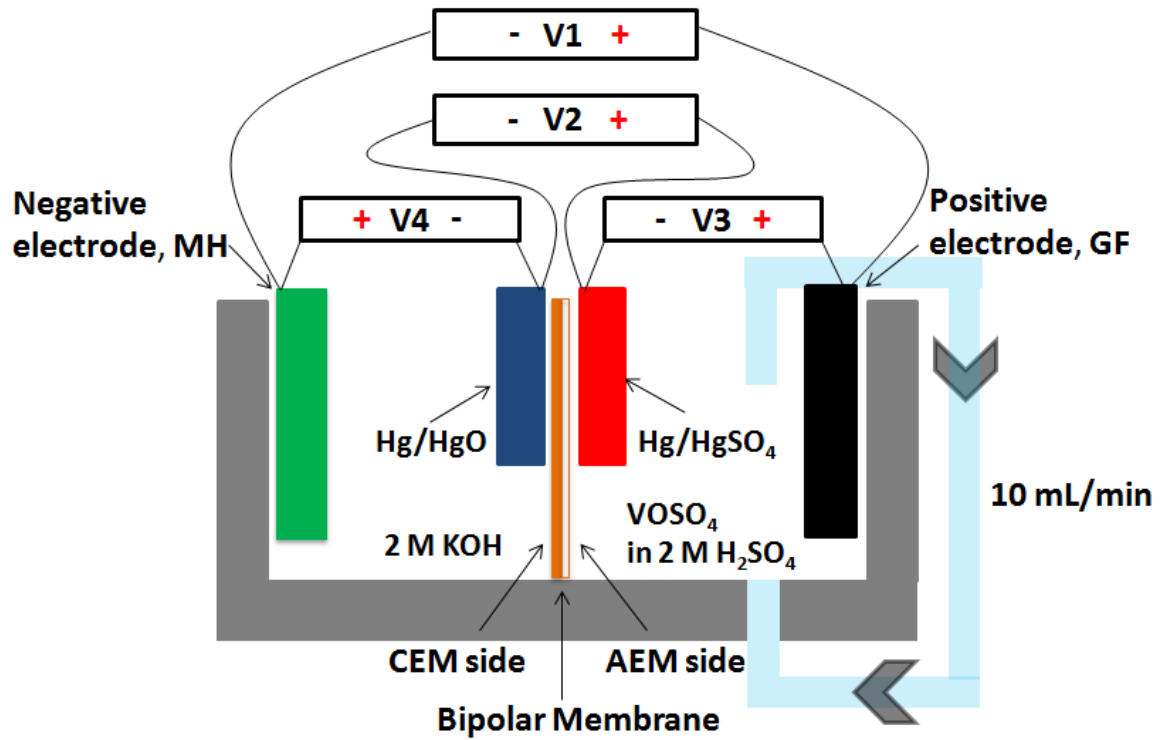
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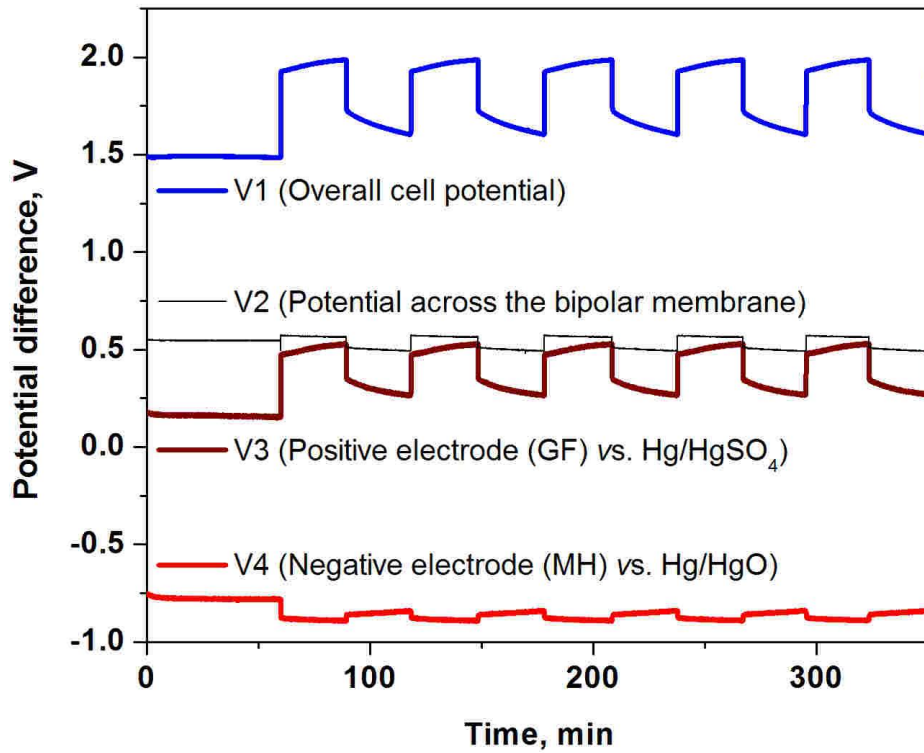
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