

FELLOWSHIP FINAL REPORT

A Vanadium Redox Flow Battery based on a highly concentrated Protic Ionic Liquid Electrolyte

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A protic ionic liquid is introduced for the first time as a solvent for a high energy density vanadium redox flow battery. The proof-of-concept redox flow cell with a concentration of 3 mol L⁻¹ vandyl sulfate electrolyte was tested for a total of 30 cycles at 40°C, showing an open circuit potential of 1.38 V, a nominal capacity of 1900 mAh at a current density of 40 mA cm⁻¹ and energy and coulombic efficiencies of 64 and 90%, respectively. The continuous 16 hours of cycling suggest that the concentrated anolyte and catholyte are thermally stable and cycleable. This study underlines a new route to improve the energy-to-volume ratio of this promising energy storage system.

1- Introduction

Considering the international pressure caused by climate change and air pollution, traditional energy sources are steadily moving towards clean energy alternatives such as solar, wind, and hydropower. Clean energy has become a multibillion-dollar industry, with solar, wind, battery, smart grid, and other sectors experiencing strong uptrends. Energy experts adjust their forecast as clean energy technologies emerge faster than predicted and are cost-competitive with coal-fired electricity and combustion-engine vehicles. Falling costs of renewables such as wind and solar PV are now "out-competing" coal worldwide, with more than 60% of existing plants currently operating at a higher cost than renewable alternatives [1]. As an example, in Germany, the introduction of the German Renewable Energy

Sources Act (2000) shifted the share of renewable energy sources in the German electricity sector from 5.2% in 1999 to 37.8% in 2018 [2].

Pumped-hydro currently dominates the (renewable) electricity storage with 96% of the installed worldwide capacity [3], followed by rapidly growing battery electrochemical storage systems. Battery storage in stationary applications looks set to grow from 2 GW worldwide in 2017 to 235 GW in 2030 [4], rivaling pumped-hydro storage. Battery storage and pumped hydro are expected to become an increasing source of overall energy turnover going forward (i.e., spot market and frequency control ancillary services market, the latter being the current principal revenue stream for batteries) [5].

Through storing energy in recirculating liquid electrolytes, redox flow batteries (RFB) are an

emerging electrochemical battery energy storage system (BESS) [6,7] for intermittent sources, primarily solar and wind. There are three main grid-based markets for this BESS, namely the grid service or in-front-the-meter, the behind-the-meter applications, and off-grid applications (e.g., island grids and remote area grids) [7]. This technology holds several merits, namely decoupled energy density and power generation capability, flexibility in system design, competence in scaling cost, and quick response time. Despite the report of several cost-effective redox-active materials that have demonstrated high solubility and fast kinetics (viz. Fe/Cr, Zn-Ce, Zn/Br₂, Fe/V, V/halide, Pb-acid, polysulfide/bromine [8,9], the most successful and commercialized RFB system is the all-vanadium redox flow battery (VRFB) [10,11]. And arguably so, the presence of the same solution as anolyte (e.g., V²⁺ and V³⁺) and catholyte (e.g., V⁴⁺ and V⁵⁺) diminishes the possibility of electrolyte cross-contamination, and the water-based electrolyte renders it non-flammable, alleviating the risk of ignition or explosion. Currently, the largest VRFB installation, rated at 200 MW/800 MWh, is Rongke Power in Dalian [8].

Positive and negative vanadium electrolytes are separately stored in tanks and individually circulated through the stack and the corresponding tanks. A proton exchange membrane separates the positive and negative sides of the VRFB. During charge, an applied voltage causes each vanadium ion to lose an electron on the positive side. The freed electrons flow through the external circuit to the negative side, where they are stored. During discharge, the stored electrons are released, flowing back through the external circuit to the positive side. Meanwhile, protons are transferred between the negative and positive electrode surfaces across the positive and negative electrolyte phases and membrane for charge balance.

In an RFB, the electric energy is stored in the electrolytes in the form of bulk fluids immersed in tanks. To increase the energy stored in this battery system, we can introduce larger reservoirs (and also the stack size) or boost the systems' volumetric capacity. The latter is

directly related to the solubility of the redox species. For the VRFB, the nature of the solvent introduced in the battery determines the solubility and stability of the numerous vanadium species of the solution. Herein we report the use of a protic ionic liquid (PIL) for the VRFB that can solubilize a markedly higher vanadyl sulfate concentration (i.e., 3 M V⁴⁺) than other VRFB electrolytes (i.e., 2 M V⁴⁺ in H₂SO₄ and/or HCl [12]).

PILs are formed by proton transfer from a Brønsted acid to a Brønsted base and represent the protic subgroup of ionic liquids. They possess a labile proton, which may participate in Faradaic reactions of proton-coupled electron transfer [13]. The ionic conductivity and supercooling character of PILs enable them to be liquid over a wide temperature window, manifested for the PIL(aq)/vanadium electrolyte between -20 and 80°C [ref.]. A proof-of-concept VRFB cell that can operate at 40°C validates the use of this green solvent for the VRFB system. This strategy can provide a platform and serve as a benchmark for the development of new generation VRFBs and, at the same time, pave the way to utilize PILs in other redox couples (e.g., Ce³⁺/Ce⁴⁺, Br₂/Br⁻ [14,15]) for RFB applications.

2- Experimental details

2.1 Materials

Pyrrolidine (>99%), methane sulfonic acid (CH₃SO₃H, >99.5%), and vanadium (IV) oxide sulfate hydrate (97.5%) were purchased from Sigma Aldrich and used without further purification. All solutions were prepared using Milli-Q deionized water (18.2 MΩ·cm).

2.2 Protic Ionic Liquid (PIL) synthesis

The PILs were synthesized according to a previously reported procedure [16]. In short, pyrrolidine was placed into a three-necked round-bottom flask equipped with a reflux condenser and a dropping funnel where methane sulfonic acid is added in a dropwise manner under rotation. The acid-base reaction is exothermic, so the temperature of the mixture was maintained at 25°C using an ice bath. Stirring was maintained for 4 h, leading to a

low-viscous liquid that was evaporated under reduced pressure. The remaining liquid was dried under vacuum using a trap with liquid nitrogen ($P = 1\text{-}5\text{ mm Hg}$). The dried salt was kept airtight under ambient conditions.

2.3 Redox flow battery

The VRFB was fabricated by sandwiching the membrane ($7\text{ cm} \times 7\text{ cm}$, Nafion 117, Ion Power Inc.) between two symmetric pieces of carbon felt (BST8-3, MTI Corporation). The geometric area of the electrodes was ca. 49 cm^2 . The ionic and contact resistances between membrane and electrode were minimized through a "zero-gap" configuration [17]. The cell was connected to the electrolyte reservoirs (volume = 40 mL) by Tygon tubing. A peristaltic pump (EQ-BK-380-2, MTI Corporation) circulated the electrolyte through the cell at a flow rate of 15 mL min^{-1} . The concentrations at the anode and cathode were $3\text{ mol L}^{-1}\text{ V}^{4+}$ and V^{3+} . First, V^{3+} and V^{5+} were generated by charging the system at a constant voltage of 1.75 V until a cut-off current of $\approx 1\text{ mA cm}^{-2}$ (i.e., 100 mA) was realized. Then, the V^{5+} electrolyte was replaced with a fresh solution of V^{4+} to reach a fully discharged state.

Prior to cycling, a potentiostat (Biologic SP150) measured the high-frequency resistance at 30 kHz using an AC potential perturbation of 10 mV amplitude. The resistance was multiplied by the active area of the membrane to yield the areal specific resistance (ASR) of the cell and to iR correct the cell potential measurements. The reported current is normalized by the geometric surface area of the electrode. Galvanostatic charge-discharge cycling was conducted through a battery analyzer (BST8-3, MTI corporation) at a normalized current density of 40 mA cm^{-2} . The cut-off limits were set at 1.8 V for charge and 0.7 V during discharge. During battery operation, nitrogen was bubbled into the negative electrolyte to prevent V^{2+} from undergoing chemical oxidation by air. A Julabo refrigerated/heating circulator (F12-MA) heated the electrolyte of the VRFB at 40°C . The temperature change between the inlet and outlet of the cell was $\pm 1.5^\circ\text{C}$.

3- Results and discussion

The physicochemical characteristics of the PIL/vanadium electrolyte have been discussed in detail in [13]. In short, the PIL(aq)/V(IV) electrolyte is i) slightly less conductive than typical aqueous electrolytes (e.g., 50 mS cm^{-1} at 40°C), ii) thermally stable on an extensive temperature range (i.e., -20 to 80°C), iii) possesses adequate viscosities (i.e., $15\text{ mPa}\cdot\text{s}$ at 40°C) and densities (i.e., 1.23 g cm^{-3}), iv) shows weak or moderate acidity compared to highly concentrated sulfuric acid solutions ($\text{pH} \approx 1.1$) and v) the anolyte and catholyte solutions (in the discharge state) are stable at 45°C for 6 weeks.

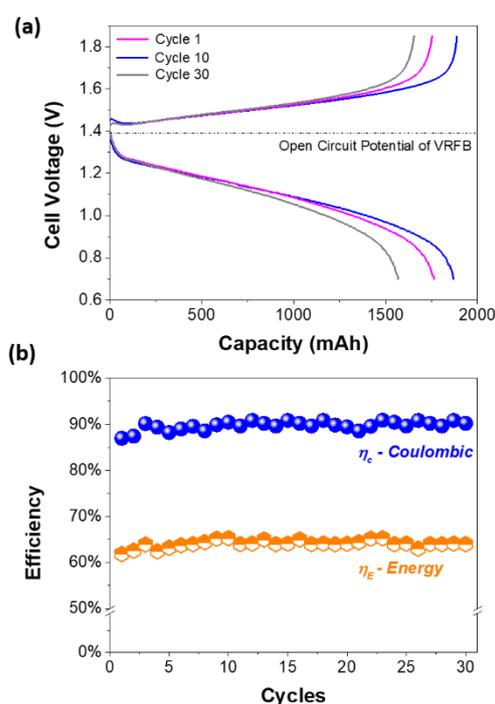


Figure 1: Performance of the VRFB at 40°C . (a) Capacity curves at 40 mA cm^{-2} . The dashed line indicates the open circuit potential of the battery cell. (b) Energy and Coulombic efficiencies over 30 cycles at 40 mA cm^{-2} .

The above results ensure that the VRFB can operate at a concentration of 3 mol L^{-1} vanadyl sulphate. To this end, we performed charge-discharge tests at the proposed concentration at a flow rate of 15 mL min^{-1} and 40°C , as elevated temperatures enhance the kinetics of the vanadium redox couples [13]. Figure 1a shows the capacity of the system at a current density of 40 mA cm^{-2} . Initially (cycle 1), the capacity reached 1900 mAh and demonstrated a

capacity retention of 87.3% for a total of 30 cycles (i.e., 16 h of continuous cycling). The open-circuit voltage of the battery reaches 1.38 V. Therefore, the volumetric energy density of the system is equal to $(96485 \text{ C mol}^{-1} \times 3 \text{ mol L}^{-1})/3600 \text{ sec}/ 1.38 \text{ V} = 58.2 \text{ Wh L}^{-1}$, superior to the traditional H_2SO_4 VRFB (35 Wh L^{-1}) [10,13]. The coulombic efficiency (η_c) of the PIL(aq) VRFB cell lingers at 90%, while the voltaic efficiency (η_v) reaches 71%, yielding an average energy efficiency (η_E) of 64% for 30 cycles (Figure 1b).

4- Conclusion

In summary, a novel protic ionic liquid electrolyte that can significantly enhance the energy density of the VRFB is reported here. To the best of our knowledge, no study concerning PIL-based electrolytes for the VRFB has been conducted so far. The proof-of-concept redox flow cell with a concentration of 3 mol L^{-1} vandyl sulfate yielded acceptable energy and coulombic efficiencies of the order of 64% and 91%, respectively, and a nominal capacity of 1900 mAh at 40 mA cm^{-2} throughout 30 cycles.

This project serves as the onset of a working platform to study several (protic) ionic liquids as suitable alternatives for redox flow battery applications and more. The aim is to gain the capability to benchmark the best-suited IL for RFB redox couples that can demonstrate i) fast kinetics, ii) large temperature window, iii) high ionic conductivity and solubility, iv) low density, and v) stability.

5- Perspectives of future collaborations with the host laboratory

Post-Fellowship collaboration with the host laboratory is already in place. The scope of the collaboration applies not only to RFB systems but also to Lithium-ion batteries (2 papers under preparation) and supercapacitors (1 paper under preparation). This corroborates the exchange of knowledge between the host and guest institutions and the intention of a long-standing collaboration between the two parties.

6- Articles published in the framework of the fellowship

The outcome of this work resulted in two papers. The first is published in the Journal of Energy Chemistry (G. Nikiforidis, A. Belhacen, M. Anouti, Journal of Energy Chemistry 57 (2021) 238-246). A following paper is under preparation.

7- Acknowledgments

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