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Leo J. Small, Harry D. Pratt, Chad Staiger, Rachel I. Martin,
Travis M. Anderson, Babu R. Chalamala

Thiagarajan Soundappan, Monika Tiwari, Venkat R. Subramanian

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Leo J. Small
Electronic, Optical, and Nano Materials (1816)
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS1411

Harry D. Pratt, Travis M. Anderson
Power Sources R&D (2546)
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0613

Rachel I. Martin, Chad Staiger
Materials, Devices, and Energy Technology (6124)
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0734

Babu R. Chalamala
Energy Storage Technology and Systems (6111)
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS1108

Thiagarajan Soundappan, Monika Tiwari, Venkat R. Subramanian
Department of Chemical Engineering
University of Washington
Box 351750
Seattle, WA USA 98185-175

Abstract

We report a simple method to synthesize V^{4+} (VO^{2+}) electrolytes as feedstock for all-vanadium redox flow batteries (RFB). By dissolving V_2O_5 in aqueous HCl and H_2SO_4, subsequently adding glycerol as a reducing agent, we have demonstrated an inexpensive route for electrolyte synthesis to concentrations >2.5 M V^{4+} (VO^{2+}). Electrochemical analysis and testing of laboratory scale RFB demonstrate improved thermal stability across a wider temperature range (-10-65 °C) for V^{4+} (VO^{2+}) electrolytes in HCl compared to in H_2SO_4 electrolytes.

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1. INTRODUCTION

With the increasing need to firm up renewable energy sources such as solar and wind, there has been a renaissance in the development of redox flow batteries (RFBs).[1,2] Though RFB systems based on the Fe-Cr redox couple were demonstrated over thirty years back,[3,4] significant commercial development occurred only after the recent development of all-vanadium RFBs.[5-7] Commercial deployment, however, has been hampered by the thermal stability and cost of their electrolyte solutions.[7,8,9,10]

Sulfuric acid based vanadium RFB systems are vulnerable to electrolyte precipitation at temperatures >40 °C.[8,12,13] Sulfate-chloride mixed acid electrolytes, though, have shown stability over -5 to 50 °C.[13-15] Nevertheless, the need for an inexpensive precursor material remains. Among vanadium oxide materials, V_2O_5 is the least expensive, based on a comparison of prices from USGS and US commercial suppliers (Sigma-Aldrich, Alfa-Aesar, etc.). Chemical reduction of V^{5+} (VO_2^+) to V^{4+} (VO^{2+}) by organic reducing agents has been proposed as a low cost route for electrolyte preparation.[16,17]

Here we present a study on the synthesis of V^{4+} species by a two step, one pot process. First, V_2O_5 is dissolved in concentrated HCl, followed by chemical reduction of V^{5+} (VO_2^+) with glycerol.[16, 17] The V^{4+} (VO^{2+}) electrolyte synthesized is subsequently used in a RFB to electrochemically generate V^{2+}/ V^{5+} species and demonstrate electrolyte cyclability and thermal stability. We prove the stability of the electrolyte across an even wider temperature range (-10 to 65°C) and compare to sulfate-based counterparts.

2. EXPERIMENTAL

In a 300 mL beaker, deionized water (38.9 mL, 2.16 mol, double distilled) and 12.1 M HCl (50.0 mL, 0.605 mol, 37% Sigma-Aldrich) were added. Under magnetic stirring, V_2O_5 (5.0 g, 0.027 mol, 99.6% Sigma-Aldrich) was added in two portions. If applicable, H_2SO_4 (99%, Sigma-Aldrich) was added. Dissolution of V_2O_5 yielded a yellow solution to which glycerol (0.7 mL 0.01 mol, 99% Sigma-Aldrich) was added dropwise with much gas violently evolved. Solution temperature was maintained within 60-90 °C for the entire process. Numerous process variations, outlined in Table 1, were performed to optimize electrolyte synthesis.

Electrolytes were evaluated in a laboratory scale RFB, with a serpentine type flow field and 5 cm^2 active area (Fuel Cell Technologies, Inc., Albuquerque, NM, USA).[18] Two carbon felt electrodes (GFD grade from SGL carbon) were separated by a DuPont Nafion-115 membrane. Electrodes were activated in air at 400 °C for 30 h, while Nafion was pretreated by sequentially boiling in deionized (DI) water for 30 minutes, soaking in 1 M H_2SO_4 for 30 minutes at 80 °C, and storing in room temperature DI water. Masterflex peristaltic pumps (Cole-Parmer, USA) maintained a flow rate of 30 mL/min. To avoid the air oxidation of V^{2+} to V^{3+}, ultra-high purity nitrogen gas was flowed over both reservoir tanks.

Cyclic voltammetry (CV) was carried out using a CH Instruments CHI-760 bi-potentiostat in a standard three electrode cell with a 3.0 mm diameter glassy carbon (GC) working electrode (CH Instruments), Ag/AgCl wire (1 M KCl) reference electrode, and a platinum wire counter electrode.

3. RESULTS AND DISCUSSION

In this two step synthesis, concentrated HCl first dissolves the V_2O_5. The addition of glycerol reduces V^{5+} (VO_2^+) to V^{4+} (VO^{2+}), yielding a mixture of HCOOH, CO, CO_2 and H_2O, as outlined in Eq. 1 and shown visually in Fig. 1a-c.[19] The resulting electrolyte solution is ready to be deployed as feedstock to generate further oxidation states (V^{5+}, V^{3+}, and V^{2+}) for RFB operation.

$$\mathrm{HOCH_2\text{-}HCOH\text{-}H_2COH} + 14\mathrm{VO_2^+} + 14\mathrm{H^+} \rightarrow 14\mathrm{VO^{2+}} + \mathrm{wH_2O} + \mathrm{xCO_2} + \mathrm{yCO} + \mathrm{zHCOOH} \quad (1)$$

Variation of the synthesis parameters in Table 1 enabled optimization of the reactant quantities for the synthesis of V^{4+} (VO^{2+}). By employing a mixed chloride-sulfate solution, VO^{2+} concentrations >2.5 M could be achieved.[13] Maintaining the reaction temperature within 60-90 °C, the reaction proceeded efficiently (~10 min), yet avoided insoluble species. At increased temperatures, the clear blue solution turned turbid, indicating the formation of unwanted, insoluble vanadium complexes.

HCl pre-diluted to concentrations less than 12 M required excessive glycerol and longer reaction times to obtain a clear blue solution characteristic of V^{4+} species. For example, with 4 M HCl, 1.4 mL glycerol and 6 h of continuous stirring and heating was required.

CV was used to evaluate the electrochemical characteristics of then synthesized V^{4+} (VO^{2+}) species.[15] Fig. 1(d) shows the CV response of the synthesized electrolyte at a GC

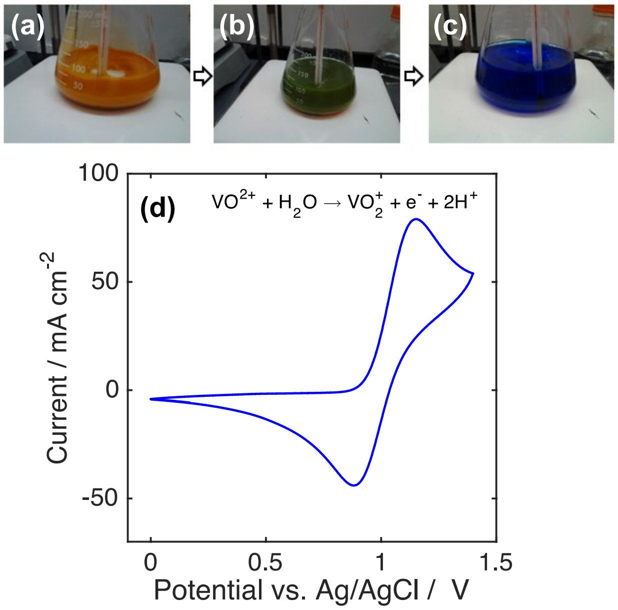

Figure 1. Stages of V^{4+} chemical synthesis: (a) Initial addition of V_2O_5 to aqueous HCl. (b) Addition of glycerol (c) Completion of glycerol-mediated reduction of V^{5+} to V^{4+}. (d) CV response of as-synthesized V^{4+} solution at a GC electrode (100 mV/s).

Glycerol / mL	DI / mL	HCl (12 M) / mL	V_2O_5 / g	Final Color
0.7	38.9	50	5.0	clear blue
1.5	“	“	“	green blue
3.5	“	“	“	dark green blue
0.7	50	50	5.0	clear blue
“	38.9	“	“	“
“	30	“	“	“
0.7	38.9	65	5.0	clear blue
“	“	50	“	“
“	“	35	“	dark black blue
0.7	38.9	50	5.0	clear blue
“	“	“	10.0	dark black blue
“	“	“	2.5	clear blue
1.7	16.8	24.8*	11.37	clear blue

*8.4 mL 99% H_2SO_4 was also added.

Table 1. Variation of reagents used in the synthesis of VO^{2+}-HCl electrolytes.

electrode. Here the peak in current attributed to V^{4+} oxidation to V^{5+} was observed at 1.151 V vs. Ag/AgCl, whereas the peak reduction current from V^{5+} to V^{4+} was observed at 0.881 V. The CV sweep began at 0.0 V and was swept anodically. A nonfaradaic current was observed until the voltage was swept sufficiently anodic for rise in oxidation current and the V^{4+} oxidation peak to be seen. This behavior, along with the deep blue color, suggests that nearly all vanadium ions were in the 4+ state, as a large V^{5+} reduction wave was not initially observed.[20]

To determine the thermal stability of vanadium chloride electrolytes, three sets of V^{4+} (VO^{2+}) solutions synthesized using 4, 8, and 12 M HCl were monitored in a temperature chamber without agitation at 65 or -10 °C for five days. No significant chemical change was observed during this period. CV studies before and after thermal treatment revealed no measurable change in the V^{4+}/V^{5+} peak potentials, confirming the electrolyte stability.

Starting with V^{4+} (VO^{2+}) in the synthesized HCl solution, a two step charging process was used to obtain V^{5+} and V^{2+}. First, 50 mL of V^{4+} (VO^{2+}) solution was placed on each side and the battery fully charged, generating V^{3+} and V^{5+} (VO_2^+). The V^{5+} (VO_2^+) solution was removed from the tank and refilled with V^{4+} (VO^{2+}). Charging the RFB again resulted in V^{3+} and V^{5+} (VO_2^+). Figure 2 shows the charge-discharge curves of V^{4+} in HCl.

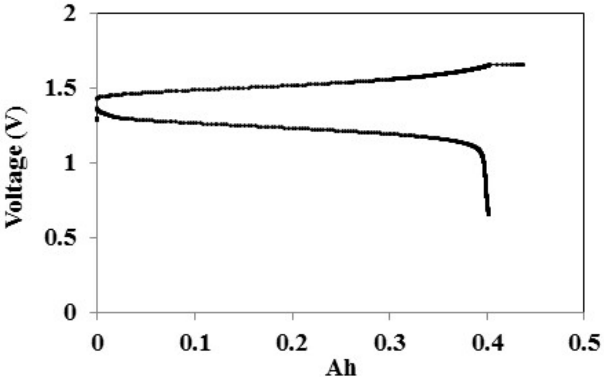

Figure 2. Charge/discharge curve of RFB with 0.6 M vanadium in 6 M HCl.

To analyze the stability of vanadium species in chloride and sulfate solutions, we utilized the previously generated V^{5+} solutions (HCl and H_2SO_4) and stored them without agitation for 95 h at 65 °C. Precipitates formed in the H_2SO_4, but not in HCl, suggesting greater stability in HCl. However, a slight color change of the HCl solution indicated partial thermal reduction of V^{5+} to

V^{4+}. Even if some of V^{5+} is thermally reduced, these species may be electrochemically reoxidized, while the precipitates in the H_2SO_4 electrolyte are no longer electrochemically active.

Using the two step charging process previously described, V^{5+} (VO_2^+) and V^{2+} were obtained in a RFB. This cell was then cycled at C/2 or 3C rate for 30 cycles. Resulting potential-time profiles and electrochemical yield (capacity fade) for the RFB cycled at C/2 are plotted in Figs. 4(a) and 4(b), respectively, while those for the 3C rate are plotted in Figs. 4(c) and 4(d). In both cases a decrease in cycling time and corresponding decrease in electrochemical yield was observed. Thus, an increasing amount of vanadium species became electrochemically inactive during cell operation. While the exact cause of this capacity fade is not clear, excess glycerol used during V^{4+} (VO^{2+}) synthesis may be reducing V^{5+} generated.

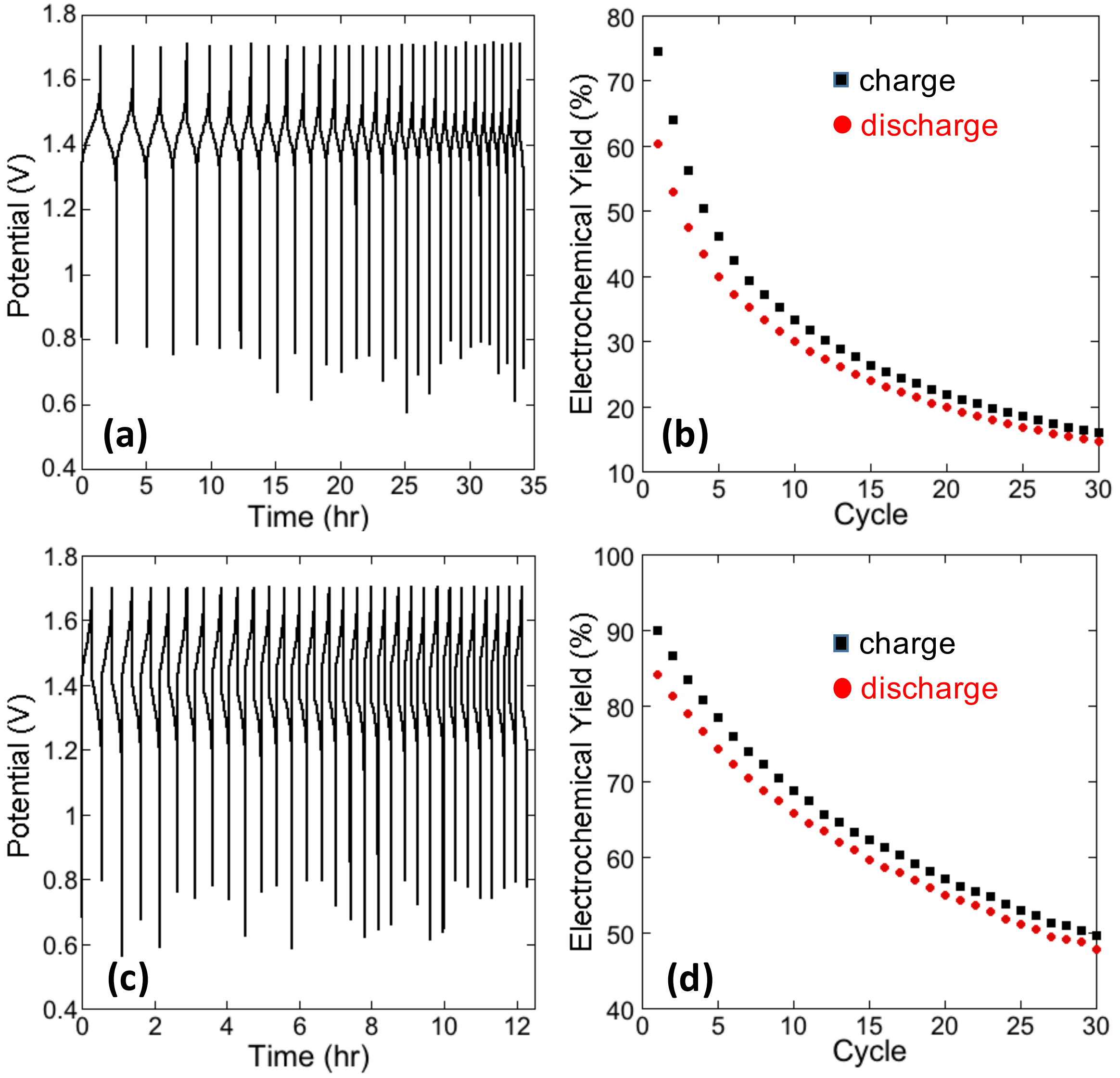

Figure 3. (a) Potential profile and (b) electrochemical yield during cycling of as-synthesized electrolyte in RFB at C/2 rate. (c) Voltage profile and (d) electrochemical yield for as-synthesized electrolyte in RFB cycled at 3C rate.

4. CONCLUSION

We have synthesized V^{4+} species from V_2O_5 precursors by a two step dissolution and chemical reduction method. The presence of HCl eliminates vanadium precipitates inherent to the V^{5+} state when coupled with SO_4^{2-} based electrolytes. At temperatures greater than 65 °C some thermal reduction of V^{5+} to V^{4+} is noted, limiting RFB efficiency in this temperature range. This chemical reduction method can be applied to mixed chloride-sulfate electrolytes, enabling >2.5 M V^{4+} (VO^{2+}). Further investigation of other organic reducing agents might enable chemical reduction to V^{3+}, allowing anolyte and catholyte to be chemically prepared separately.

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