



# Non-aqueous chromium acetylacetonate electrolyte for redox flow batteries

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## ABSTRACT

A single-metal redox flow battery employing chromium(III) acetylacetonate in tetraethylammonium tetrafluoroborate and acetonitrile has been investigated using electrochemical techniques. Cyclic voltammetry was used to evaluate electrode kinetics. Four redox couples were observed in the stable potential window. The Cr<sup>II</sup>/Cr<sup>III</sup>, Cr<sup>I</sup>/Cr<sup>II</sup>, Cr<sup>III</sup>/Cr<sup>IV</sup> and Cr<sup>IV</sup>/Cr<sup>V</sup> redox couples all appeared to be quasi-reversible, with the Cr<sup>III</sup>/Cr<sup>IV</sup> couple exhibiting comparatively slow kinetics. A cell potential of 3.4 V was measured for the one-electron disproportionation of the neutral Cr<sup>III</sup> complex. The diffusion coefficient for chromium acetylacetonate in the supporting electrolyte solution was estimated to be in the range of 5.0–6.2 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup> at room temperature. The charge–discharge characteristics of this system were evaluated in an H-type glass cell, and coulombic and energy efficiencies of approximately 55% and 20%, respectively, were obtained.

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## 1. Introduction

Redox flow batteries (RFBs) differ from conventional batteries in that they store chemical energy in two liquid electrolytes, rather than in solid electrodes. To implement battery charge or discharge, these electrolytic solutions are pumped through a power-conversion reactor that oxidizes and reduces the dissolved active materials. RFBs are not susceptible to self-discharge because the anolyte and catholyte are physically separated. Since the electrodes act primarily as electron donors or acceptors, RFB systems are free of the cycle-life limitations associated with mechanical fatigue in conventional battery electrodes. Thus RFBs are being developed for grid-level applications, to store the large amounts of energy generated by intermittent power systems such as wind turbines or solar cells.

Several RFB chemistries have been developed, which are classified by the active species employed. Examples include iron–chromium [1], all–vanadium [2,3], vanadium–bromine [4], and bromine–polysulfide [5] RFBs, all of which are aqueous chemistries. The cell potential of aqueous RFBs must lie within the electrochemical stability range of water. Since the cell potential determines energy and power densities, aqueous chemistries limit system performance. In addition, the water in an RFB limits operating temperatures to approximately 0–100 °C.

Non-aqueous electrolytes promise wider stable potential windows, wider operating temperature ranges, and higher energy and

power densities than aqueous electrolytes. A few non-aqueous RFB chemistries have been reported previously. Matsuda et al. evaluated a redox system based on a ruthenium bipyridine complex, which yielded a cell potential of 2.6 V [6]. Chakrabarti et al. studied ruthenium acetylacetonate, obtaining a cell potential of 1.77 V [7]. Yamamura et al. investigated non-aqueous redox systems based on various uranium beta-diketonates, which afforded cell potentials of ~1 V [8]. Recently, Thompson and co-workers demonstrated an RFB system using vanadium acetylacetonate, observing a cell potential of 2.2 V [9].

This paper describes a single-metal non-aqueous redox system based on chromium(III) acetylacetonate (Cr(acac)<sub>3</sub>) active species, supported by tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) in acetonitrile (CH<sub>3</sub>CN). Chromium complexes have previously been studied for use in aqueous RFBs [10] but this is the first report of their use in single-metal non-aqueous RFBs. Cyclic voltammetry (CV) was used to evaluate the cell potential and kinetic rates. Charge–discharge characteristics were determined using an H-type cell with an anion-exchange membrane separator.

## 2. Experimental

### 2.1. Electrolytes

Electrolytic solutions were prepared by dissolving Cr(acac)<sub>3</sub> (97.5%, Strem, U.S.) and TEABF<sub>4</sub> (99%, Fluka, U.S.) in anhydrous CH<sub>3</sub>CN (99.8%, Aldrich, U.S.). The Cr(acac)<sub>3</sub> and TEABF<sub>4</sub> concentrations were 0.05 M and 0.5 M, respectively.

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## 2.2. Cyclic voltammetry

Cyclic voltammetry was performed using an Autolab PGSTAT302N Potentiostat/Galvanostat (Ecochemie, Netherlands). A 3 mm diameter glassy carbon working electrode (BASi, U.S.) was used. The working electrode was polished according to the method of Liu et al. [9]. Potentials during CV were measured relative to a 0.01 M Ag/Ag<sup>+</sup> and 0.1 M TEAClO<sub>4</sub> reference electrode, which was connected to the working-electrode chamber via a Luggin capillary. A large-area (~9 cm<sup>2</sup>) graphite plate (Graphitstore, U.S.) was used as the counter electrode. Solutions were purged with research-grade nitrogen prior to experiments.

## 2.3. Charge–discharge experiments

An H-type glass cell was used for charge–discharge experiments [7,9]. Both compartments contained 10 mL of electrolytic solution and were continuously agitated using Teflon magnetic stir-bars. The electrolytes were separated by a Neosepta AHA anion-exchange membrane (Astom, Japan). Prior to each experiment, the membranes were pre-conditioned by soaking in a solution containing 0.5 M TEABF<sub>4</sub> and CH<sub>3</sub>CN for more than 22 h. Two graphite electrodes were employed in the charge–discharge experiments, with immersed surface areas of 7 cm<sup>2</sup>. Galvanostatic charge and discharge currents were 1.0 mA and 0.1 mA, respectively. Charge cycles were run up to 50% of the theoretical maximum state of charge (SOC), and discharge cycles down to 0.1 V. All of the charge–discharge experiments were performed in an argon-filled glove box.

## 3. Results and discussion

### 3.1. Voltammetric behavior of Cr(acac)<sub>3</sub> in acetonitrile

Fig. 1 shows the CV for a solution containing 0.05 M Cr(acac)<sub>3</sub> and 0.5 M TEABF<sub>4</sub> in CH<sub>3</sub>CN cycled at 50 mV s<sup>-1</sup>. Four redox couples were observed within the solvent stability window. Chromium acetylacetonate electrochemistry has been reported previously [11–15]. Landsberg et al. defined the Cr(acac)<sub>3</sub> reduction potentials in dimethyl sulfoxide (DMSO) [13]. They observed two redox couples at reductive potentials and attributed them to one-electron reductions of the Cr(acac)<sub>3</sub> complex. Although the absolute values of these reduction potentials are difficult to compare with potentials reported here (due to differences in the reference electrodes used and different solvents), the voltage difference between the first and second reductions appears similar to that observed in our work (300–400 mV). We

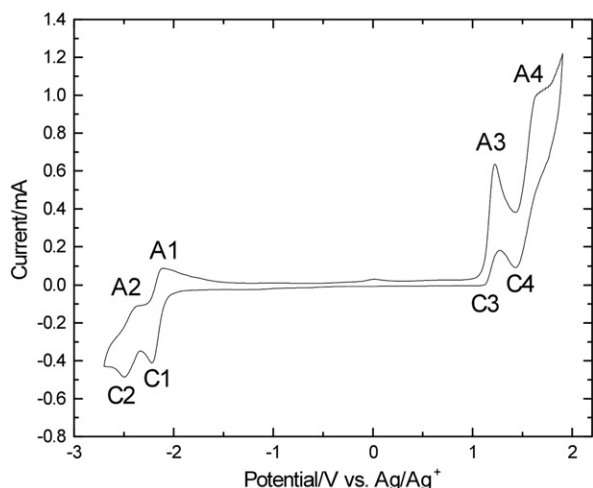


Fig. 1. Cyclic voltammograms measured at a glassy carbon electrode in 0.05 M Cr(acac)<sub>3</sub> and 0.5 M TEABF<sub>4</sub> in CH<sub>3</sub>CN; scan rate 50 mV s<sup>-1</sup>; room temperature.

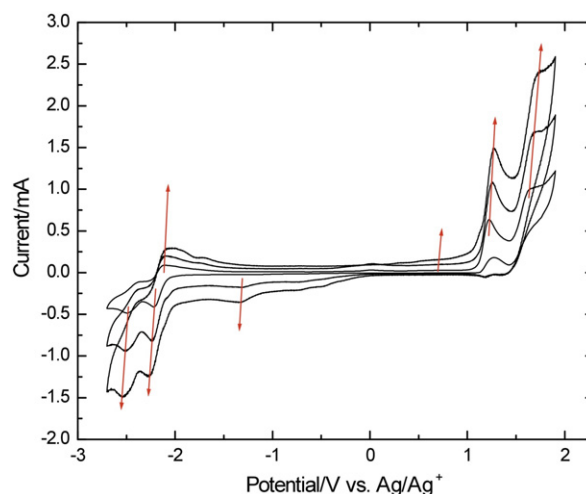
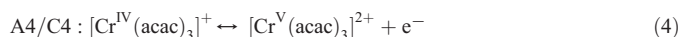
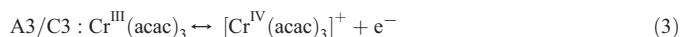


Fig. 2. Cyclic voltammograms measured at a glassy carbon electrode in 0.05 M Cr(acac)<sub>3</sub> and 0.5 M TEABF<sub>4</sub> in CH<sub>3</sub>CN at scan rates of 50, 200, and 500 mV s<sup>-1</sup>, arrows show direction of increasing scan rate; room temperature.

have therefore attributed the redox couples observed at reductive potentials to the following reactions:



The redox couples observed at oxidative potentials are consequently attributed to:



Features on the CV associated with redox half-reactions (1)–(4) are labeled on Fig. 1.

Formal potentials for each half-reaction were estimated by averaging the anodic and cathodic peak potentials. These formal potentials indicate that an RFB system based on one-electron disproportionation of Cr(acac)<sub>3</sub> would yield a 3.4 V equilibrium cell potential. This is approximately 2.5× higher than the potential reported for aqueous vanadium RFBs (1.26 V under standard conditions [16]). The cell potential could be as high as 4.1 V if it is possible to induce the two-electron disproportionation of Cr(acac)<sub>3</sub> reversibly.

### 3.2. Kinetics of electrode reactions

Fig. 2 shows a series of CVs at various scan rates for electrolytic solutions containing 0.05 M Cr(acac)<sub>3</sub> and 0.5 M TEABF<sub>4</sub> in CH<sub>3</sub>CN. For the Cr<sup>II</sup>/Cr<sup>III</sup> and Cr<sup>I</sup>/Cr<sup>II</sup> couples, associated with reduction of the neutral complex, the peak separation  $\Delta E_p$  increased slightly with increasing scan rate. The ratios of anodic to cathodic peak currents were near unity for both reduction couples, suggesting quasi-reversible electrode kinetics for reactions (1) and (2). A peak near 1.2 V vs. Ag/Ag<sup>+</sup> associated with the Cr<sup>III</sup>/Cr<sup>IV</sup> reduction (C3 on Fig. 1) only appeared at higher scan rates. Below 100 mV s<sup>-1</sup>, the reduction sweep of the voltammogram was essentially sigmoidal between 1.3 and 1.0 V vs. Ag/Ag<sup>+</sup>, suggesting very sluggish kinetics. Peak separation for the Cr<sup>IV</sup>/Cr<sup>V</sup> redox couple increased slightly with increasing scan rate. As with reactions (1) and (2), reactions (3) and (4) show quasi-reversible kinetics.

The CVs in Fig. 2 also show small reduction and oxidation peaks near -1.25 V and 0.5 V vs. Ag/Ag<sup>+</sup>, respectively, which become more prominent with increasing scan rate. The origin of these features has not been determined unambiguously; preliminary experiments suggest

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