Temperature-dependent study of AcFc-Fe$^{\text{III}}$(acac)$_3$ redox couple for non-aqueous redox flow battery

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Abstract

This article describes the temperature dependence electrochemical analysis of acetyl ferrocene (AcFc) and iron(III) acetylacetonate ([Fe(acac)$_3$]) for non-aqueous redox flow batteries. An electrochemical cell consisting of AcFc and ([Fe(acac)$_3$]) as catholyte and anolyte species, respectively, were constructed with a cell voltage of 1.41 V and Coulombic efficiencies >99% for up to 50 total cycles at 25°C (RT) and 0°C. Rotating ring disk electrode (RRDE) experiments suggest that diffusion coefficient decreases as the temperature decreases but overall storing capacity far better than aqueous redox flow battery (ARFBs). The electrochemical kinetic rate constant ($k_0$) of AcFc was found larger than Fe(acac)$_3$ but remains similar at both temperatures. NMR study shows no structural change in changing temperature and after battery experiments.
Keywords: Nonaqueous redox flow battery, Anolyte, catholyte, Acetyl Ferrocene, Iron(III)acetyladionate,

Introduction
Fossil fuel depletion, a harmful effect of greenhouse gas emission and future energy demand, requires an essential transition from hydrocarbon fuel to renewable and environmentally friendly energy sources.¹⁻³ Solar and wind energy are the most abundant and accessible renewable energy, however, they are not available all the time. Environmental factors such as bad weather, intermittent, variable, and diffuse natures make renewable energy unavailable.¹ Deployment of renewable energy as the main energy source in power grids requires low-cost, scalable energy storage. Energy storage is a vital part of successful renewable energy implementation. Redox flow batteries are promising to fulfill all of these requirements.⁴⁻⁶ Vanadium-based aqueous redox flow batteries (ARFBs) are one of the primary responses to the grid-level energy storages. However, ARFBs suffer from numerous drawbacks, e.g., low energy density (∼50 W·h L⁻¹), limited operational temperatures (0–100 °C), and a narrow electrochemical window (1.23 V).⁷ To overcome those limitations, non-aqueous redox flow batteries were introduced to the energy storage community. A simple schematic diagram of NARFBs is shown in Figure 1. In charge mode, the catholyte oxidizes while the anolyte reduces and in discharge mode, the opposite
reaction occurs. Anolyte and catholyte continuously flow to the fuel cell by the pump. Anolyte and catholyte tanks can be scaled upon demand.

**Figure 1.** Schematic diagram of 1e⁻ system Redox flow battery. C.M is a catholyte molecule and A.M is an anolyte molecule.

Acetonitrile (MeCN) is one of the best nonaqueous solvents for NARFBs because of its wide potential window (5 V) and freezing point is -45°C. ARFBs are useless at low temperature because of water freezing point is 0°C. At this temperature or lower MeCN based RFBs could perform effectively without any freezing. NARFBs that are competitive with vanadium RFBs in all performance indicators (e.g. solubility >1.0 M, voltage output > 1.0 V, and cycling longevity >10000 cycles) remain a challenge.⁸,⁹ Recently many people are focusing on organic analytes, catholyte-based NARFBs.⁴,¹⁰–¹² But inorganic metal complex anolyte and catholyte are more stable in terms of longevity. Different metals like V, Cr, Mn, Co, Cu, and Ni complexes bearing acetylacetonate (acac), dithiolate, dithiolene, 2,2’-bipyridine (bpy), and cyclopentadienyl ligands have lately gained attention as electrolytes for NRFBs.¹³–¹⁵ To increase the number of electrons
stored per molecule, most of the studies have focused on the two 1e⁻ redox couples. Some Ni and thiocarbamate-based complexes also showed a good possibility in NARFBs. However, to date, none of these complexes has fulfilled all the requirements. Acetylferrocene (AcFc) is a one-electron system, which has a high solubility in MeCN at RT and 0°C, high cyclic longevity, and can be used as catholyte in NARFBs. Iron (III) acetylacetonate ([Fe\textsuperscript{III}(acac)\textsubscript{3}]), is also a one-electron system, which has also high solubility in MeCN at RT and 0°C, high cyclic longevity, and can be used as anolyte in NARFBs.

Herein, this study presents AcFc-[Fe\textsuperscript{III}(acac)\textsubscript{3}] redox couple temperature dependence study in MeCN to be used as an effective electrolyte in the NARFBs. AcFc and [Fe\textsuperscript{III}(acac)\textsubscript{3}] analyzed by cyclic voltammetry (CV) and rotating ring disk electrode experiments at room temperature (RT) and 0°C. These studies suggest using AcFc-[Fe\textsuperscript{III}(acac)\textsubscript{3}] redox couple as an electrolyte in NARFB experiment can achieve all requirements (e. g. solubility >1.0 M, voltage output > 1.0 V, and cycling longevity >10000 cycles). Battery experiments were also performed at RT and 0°C. AcFc-[Fe\textsuperscript{III}(acac)\textsubscript{3}] redox couples can maintain coulombic efficiency up to 99% at both temperatures.

**Experimental**

**Chemicals and Instrument**

Ethanol, tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) were purchased from Sigma-Aldrich. TBAPF\textsubscript{6} was recrystallized and dried by following the conventional method and preserved in a vacuum oven for further use.\textsuperscript{18,19} 0.1 M TBAPF\textsubscript{6} in acetonitrile was used as a solvent for cyclic voltammetry (CV) and battery experiments. The solution was degassed by nitrogen to remove the effect of oxygen on the redox properties of electrolytes. Acetyl Ferrocene (AcFc, 99.9%) and Iron (III) acetylacetonate ([Fe(acac)\textsubscript{3}], 99.9%) were also purchased from Sigma-Aldrich and used as it is. The temperature was controlled and monitored by Julabo 601F Chiller.
and ethanol was used as circulating solvent. CV experiments temperature was controlled by doing experiments in jacketed model Garry echem cell. Wave Driver 20 bipotentiostat (Pine Research) was used for the CV experiments. CHI potentiostat was used for battery experiments in the H cell and temperature was controlled by placing the H cell in the chiller solvent bath. NMR experiments were done in Bruker 500 MHz at 25°C and 0°C.

**Electrochemistry**

The working electrode was made up of by glassy-carbon (GC)-disk (5 mm diameter, Pine Research), an Ag/ Ag+ nonaqueous solution with 0.001 M AgNO₃ in MeCN (BASi Research Products) played the role of the reference electrode. The counter electrode was a platinum wire (Pine Research). To clean the electrode 0.05 μm water−alumina slurry (Allied High-Tech Products Inc., deagglomerated) and polishing pad (Buehler) were utilized before and after each experiment. The consistency of the obtained result was checked by measuring the reduction potential of ferrocene (Fc, Alfa Aesar, 99%) as a standard before and after every electrochemical experiment. The resistance of the internal solution was adjusted for all experiments. The scanning was conducted in a positive direction for AcFc and negative direction for Fe(acac)₃, where each experiment contained three continuous cycles, and data from the third cycle was considered for the analysis. Rotating disk electrode (RDE) experiments were done to calculate electrokinetic parameters.

**Battery Experiment**

This experiment was performed by following the similar method of Kowalski et al.,(ref) where a custom-made H-cell was utilized. AMI 7001 anion exchange membrane (Fuel cell) was used to separate the electrolyte of two chambers of H-cell. The working and counter electrode was made by carbon felt (Fuel cell) and was separately placed in two different chambers. The reference electrode was placed next to the working electrode and made by Fritted Ag/Ag+, contained 10 mM
AgNO₃ in 0.1 M TBAPF₆/MeCN. The electrolyte electrode is 3.5 mL of 10 mM neutral active species (MEEPT, DMeOECz, DDB, and BECP-BF₄) in 0.1 M TEABF₄/ACN. The voltage boundaries for each active species were as follows; AcFc: 1.2-0.3 V, Fe(acac)₃: -0.1--1.1 V vs. Ag/Ag⁺. Continuous stirring was used in both working and counter electrode chambers to ensure the necessary mass transfer as well as completion of the charging-discharging cycle. The applied anodic current was 2 mA and the cathodic current was 1 mA, respectively.

Results and Discussion

AcFc CV studies were performed with 1 mM AcFc in MeCN with 0.1 M TBAPF₆ electrolyte at RT or 25°C and 0°C. Figure 2 (a) shows representative voltammograms for AcFc collected at scan rate over a range of 50-3000 mV at RT. All data was collected as an oxidation step first followed by a reduction step. Redox potential (E½) of AcFc was found to be 0.8 V. This positive redox potential suggests AcFc as a potential candidate for catholyte in NARFB. Higher catholyte redox potential provides high cell voltage. CV data suggest that there is no chemical step involved in the redox cycle of AcFc and only the electron transfer step occurs. Based on the current intensity it indicates reversible 1e⁻ oxidation and reduction peaks produced by AcFc. Figure 2(a) inset shows how the cathodic current (-ipc) and anodic current (ipa) ratio change with the scan rate change. It can be seen that over the all-scan rate (-ipc/ipa) ratio remains constant around 0.83 which indicates a reversible redox couple. Although the theoretical perfect reversible redox couple (-ipc/ipa) ratio is 1.
Figure 2. (a) CV data normalized by (scan rate)$^{-1/2}$ for 1 mM AcFc. a) Scan rate range 50-3000 mV/s, (a) inset cathodic current ($i_{pc}$) and anodic current ($i_{pa}$) ratio vs scan rate ($v$) plot. b) Anodic and cathodic current vs (scan rate)$^{-1/2}$ plot. All data collected in MeCN with 0.1 M TBAPF$_6$ at RT or 25 °C.

Figure 2(b) shows how cathodic current ($i_{pc}$) and anodic current ($i_{pa}$) changes with the square root of scan rate ($v$). Both $i_{pc}$ and $i_{pa}$ linearly change with the $v^{1/2}$ with $R^2$ value 0.999. This kind of behavior indicates that the AcFc/AcFc$^+$ redox couple is a diffusion control system. AcFc CV data and $i_{pc}$, $i_{pa}$ vs $v^{1/2}$ at 0 °C are shown in Figure S 1. CV data indicates that at high scan rate reversibility decreases or peaks broadens due to diffusion of AcFc at the electrode surface from the bulk as Figure S 1 (b) linear plot suggests. Adding more supporting electrolytes to the system may increase the diffusion or increase the flow rate in the real redox flow battery experiment.

$Fe^{III}(acac)_3$ CV studies were also performed with 1 mM $Fe^{III}(acac)_3$ in MeCN with 0.1 M TBAPF$_6$ electrolyte at RT and 0 °C. Figure 3 (a) shows representative voltammograms for $Fe^{III}(acac)_3$ collected at scan rate over a range of 50-2500 mV. All the data was collected as a reduction step first followed by an oxidation step. Redox potential ($E_{1/2}$) of $Fe^{III}(acac)_3$ was found to be -0.61 V. This negative redox potential suggests $Fe^{III}(acac)_3$ as a potential candidate for anolyte in NARFB.
Lower anolyte redox potential provides high cell voltage. CV data suggest that there is no chemical step involved in the redox cycle of Fe\textsuperscript{III}(acac)\textsubscript{3} and only the electron transfer step occurs. Although at a high scan rate the reduction peak broadens due to diffusion-controlled charge transfer. Based on the current intensity it indicates reversible 1e\textsuperscript{-} reduction and oxidation peaks produced by Fe\textsuperscript{III}(acac)\textsubscript{3}. Figure 3(a) inset shows how the anodic current (i\textsubscript{pa}) and cathodic current (-i\textsubscript{pc}) ratio changes with the scan rate change. Over the scan rate (-i\textsubscript{pc}/i\textsubscript{pa}) ratio remains constant at around 0.80 which indicates a reversible redox couple.

**Figure 3.** (a) CV data normalized by (scan rate)\textsuperscript{-1/2} for 1 mM Fe\textsuperscript{III}(acac)\textsubscript{3} a) Scan rate range 50-2500 mV/s, (a) inset cathodic current (-i\textsubscript{pc}) and anodic current (i\textsubscript{pa}) ratio vs scan rate (v) plot (b) Anodic and cathodic current vs (scan rate)\textsuperscript{-1/2} plot. All data was collected in MeCN with 0.1 M TBAPF6 at RT or 25\textdegree C.

**Figure 3(b) shows how cathodic current (-i\textsubscript{pc}) and anodic current (i\textsubscript{pa}) changes with the square root of scan rate (v). Both i\textsubscript{pc} and i\textsubscript{pa} also linearly change with the v\textsuperscript{1/2} with R\textsuperscript{2} value 0.997. This kind of behavior indicates that the Fe\textsuperscript{III}(acac)\textsubscript{3}/ Fe\textsuperscript{II}(acac)\textsubscript{3} redox couple is a diffusion-controlled system. Fe\textsuperscript{III}(acac)\textsubscript{3} CV data and i\textsubscript{pc}, i\textsubscript{pa} vs v\textsuperscript{1/2} at 0\textdegree C are shown in Figure S 2. Like AcFc Fe\textsuperscript{III}(acac)\textsubscript{3} CV
data also clearly indicates that at high scan rate reversibility decreases or peaks broadens but more due to diffusion of Fe\textsuperscript{III}(acac)\textsubscript{3} at the electrode surface from the bulk as Figure S 1 (b) linear plot describes. Here, the peak current ratio is around 0.6 in comparison to the 0.8 of AcFc at 0 °C. Fe\textsuperscript{III}(acac)\textsubscript{3} electron transfer rate slightly falls at a lower temperature.

**RRDE** experiments were done in shielding mode where center disk potential was held at a certain potential to oxidize AcFc and to reduce Fe(acac)\textsubscript{3} and ring potential changed to collect limiting current.\textsuperscript{26} Figure 4(a) shows AcFc disk and ring limiting current at different rotations by holding disk potential at 1.1 V. With this potential AcFc oxidizes to AcFc\textsuperscript{+} at the disk and reduces back to AcFc at the ring. From the limiting current and rotation rate, the Koutecký-Levich plot was generated (Figure 4(a) inset). From the slope of Koutecký-Levich plot diffusion coefficient calculated by using the following Koutecký-Levich **Equation 1.**\textsuperscript{27,28}

\[
\frac{1}{i} = \frac{1}{i_k} + \left( \frac{1}{0.62 \ n \ F \ A \ C \ D^{2/3} \ \nu^{-1/6}} \right) \ \omega^{1/2} \tag{1}
\]

Where, i is the limiting current on the disk, n is the number of electrons, F is the Faraday constant (96485 C mol\textsuperscript{-1}), D is the diffusion coefficient, ν is the kinematic viscosity (taken here as 4.27E\textsuperscript{3} cm\textsuperscript{2}/s), ω is the rotation rate (rad s\textsuperscript{-1}), C is the bulk concentration electrolyte (taken here as 1E\textsuperscript{3} moles/L), and A is the disk area (GC-disk RRDE 0.1963 cm\textsuperscript{2} and Pt-ring RRDE is 0.1642 cm\textsuperscript{2}). Diffusion coefficient for ACFc at 25° C is 2.43E\textsuperscript{-5} cm\textsuperscript{2}/s. Similarly Figure 4(b) shows for AcFc at 0° C and the calculated diffusion coefficient is 2.2E\textsuperscript{-5} cm\textsuperscript{2}/s. Figure 4(c) and Figure 4(d) presents Fe(acac)\textsubscript{3} data at 25° C and 0° C respectively. Diffusion coefficient for Fe(acac)\textsubscript{3} at 25° C is 3.12E\textsuperscript{-5} cm\textsuperscript{2}/s and at 0° C 1.92E\textsuperscript{-5} cm\textsuperscript{2}/s. It was found that the diffusion coefficient values are
within the same order of magnitude and larger than those of the most reported electroactive species in NARFBs. For both electrolyte diffusion coefficient values decrease with the temperature drops which suggests that at lower temperature diffusion decreases. Fe(acac)_3 D value change is much bigger than AcFc.

**Figure 4.** (a) AcFc ring limiting current by holding disk potential at 1.1 V at 25° C. inset- Koutecký-Levich plot. (b) AcFc ring limiting current by holding disk potential at 1.1 V at 0° C. inset- Koutecký-Levich plot. (c) Fe(acac)_3 ring limiting current by holding disk potential at -0.95 V at 25° C. inset- Koutecký-Levich plot. (d) Fe(acac)_3 ring limiting current by holding disk potential at -0.95 V at 0° C. inset- Koutecký-Levich plot.
Using Koutecky–Levich Equation 1 we can calculate heterogeneous electron transfer rate constant \((k^0)\) for AcFc and Fe(acac)₃ at both temperatures. In the case of D value calculation, we have taken plateau limiting current and here we have taken not plateau current. Here, \(i_k\) is the kinetic-controlled current any mass-transfer effects are absent and is dependent on the reaction kinetics. \(i^{-1}\) vs \(\omega^{1/2}\) Koutecky–Levich plot intercept is \(1/i_k\) and Tafel plot \((\log(i_k) vs\overpotential)\) generated using the acquired values, yielding a y-axis intercept that equals the \(\log(i_0)\). The reaction rate constant \((k_o)\) can be calculated using Butler–Volmer analysis (Equation 2), where \(n\) is the number of electrons, Faraday’s constant \(F = 96485 \text{ C mol}^{-1}\), electrode area \(A = 0.1963 \text{ cm}^2\), and \(C\) is the concentration \(1 \text{ mM}\).

\[
i_o = n F A k C
\]  

\text{Equation 2}
Linearly fitted Koutecky–Levich plots of $i^{-1}$ as a function of the square root of the rotation rate ($\omega$) under different overpotentials ($\eta$). (Inset) Linearly fitted plots of $\log i_k$ as a function of the overpotential ($\eta$). (a) AcFc at 0°C, (b) AcFc at 25°C, (c) Fe(acac)$_3$ at 0°C, (d) Fe(acac)$_3$ at 25°C.

AcFc electrochemical kinetic rate constant ($k_o$) at 25°C and 0°C were calculated to be $1.1 \times 10^{-2}$ cm s$^{-1}$ and $1.3 \times 10^{-2}$ cm s$^{-1}$ respectively, for the oxidation reaction of AcFc. Similarly, $k_o$ of Fe(acac)$_3$ at 25°C and 0°C were calculated to be $3.3 \times 10^{-3}$ cm s$^{-1}$ and $1.3 \times 10^{-3}$ cm s$^{-1}$ respectively, for the reduction of Fe(acac)$_3$. This kinetic parameter of AcFc is greater than Fe(acac)$_3$, is therefore expected to lead to fast electron transfer processes in the battery test.

**Battery Experiment** was performed in a three-electrode system H cell and placing the H cell in a chiller solvent bath. Figure 6 (Top) shows battery experiment charge-discharge cycle 7 h data using AcFc as catholyte and Fe(acac)$_3$ as anolyte in 0.1 M TBAPF6-MeCN at RT. Charge applied current is 2 mA and the discharge applied current is 1 mA. The full 50 cycle charge-discharge plot is shown in Figure S3. At around 0.4 V potential charging starts and completes at around 0.5 V. In contrast, discharge starts at 0.45 V and completes at 0.35 V.
Figure 6 RT data. (Top) Battery experiment charge-discharge cycle using AcFc as catholyte and Fe(acac)$_3$ as anolyte in 0.1 M TBAPF$_6$-MeCN. Charge applied current is 2 mA and the discharges applied current is 1 mA. (bottom) How to charge/discharge/coulombic efficiency changes over the 50 cycles.

Figure 6 (Bottom) shows how to charge/coulombic efficiency charges over the 50 cycles in around 14h experiment at RT. It can be seen that after 50 cycles around 15% charge decreases even though coulombic efficiency remains 99% over the full 14 h period. Here charge fading happens in both charging and discharging mode. Discharging efficiency is 100% but cycle after cycle charging efficiency decreases. It could be because of either crossover of electrolytes, decaying of electrolytes, or diffusion of electrolytes. Different membrane-based and flow system experiments could improve charge fading.
Figure 7 0°C data. (Top) Battery experiment charge-discharge cycle using AcFc as catholyte and Fe(acac)_3 as anolyte in 0.1 M TBAPF_6-MeCN. Charge applied current is 2 mA and the discharges applied current is 2 mA. (bottom) How to charge/discharge/coulombic efficiency changes over the 50 cycles.

Battery experiment charge-discharge cycle 7 h data using AcFc as catholyte and Fe(acac)_3 as anolyte in 0.1 M TBAPF_6-MeCN at 0°C shown in Figure 7 (Top). Charge applied current is 2 mA and the discharge applied current is 2 mA. The full 50 cycle charge-discharge plot is shown in Figure S4. At around 0.4 V potential charging starts and completes at around 0.5 V. In contrast, discharge starts at 0.45 V and completes at 0.35 V. At 0°C charge-discharge capacity fading is higher than RT Figure 7 (Bottom). Over 11 h 50 cycles 26% charge capacity dropped because of
low mass transport or diffusion even though coulombic efficiency remains around 99%. CV and RRDE experiments also indicate lowering diffusion or mass transport.

NMR spectrum of both AcFc and Fe(acac)₃ was collected at 25°C and 0°C to see whether any change occurs or not by changing temperature. Figure S5-6 shows the NMR spectrum of AcFc and Figure S7 shows Fe(acac)₃ NMR spectrum. In both cases, there was no change observed in the NMR spectrum. In Fe(acac)₃ NMR only solvent (at 1.96 ppm) and water (2.16 ppm) peaks are observed because Fe(III) is d⁵ paramagnetic. As a result of the paramagnetic peak broadening, the NMR signal was not observable. AcFc four characteristic peaks (at 2.38, 4.23, 4.54, and 4.77 ppm) were observed at both temperatures. Figure 8 shows NMR data before and after battery experiments in presence of supporting electrolyte TBAPF6. The peak at around 1.96 ppm is for solvent and at 2.16 ppm is for water. Four peaks at 0.98, 1.38, 1.62, and 3.09 ppm correspond to TBAPF₆. Figure 8 (a) shows AcFc data and Figure 8 (b) shows Fe(acac)₃ data. It can be seen that no extra peak was observed after battery experiments which indicates no degradation occurred during the electrochemical oxidation and reductions. This NMR data reveals the stability of AcFc as a catholyte and Fe(acac)₃ as an anolyte in a non-aqueous redox flow battery.
Figure 8 NMR data collected before and after battery experiments. (a) AcFc in presence of supporting electrolyte TBAPF$_6$ data (b) Fe(acac)$_3$ data in presence of TBAPF$_6$.

Conclusions
A set of redox couple (AcFc and Fe(acac)$_3$) temperature-dependent electrochemical analyses were done and used as catholyte and anolyte in redox flow battery at RT and 0$^\circ$C. Total 1.41 V cell voltage was constructed with these redox couples as AcFc redox potential was found to be 0.8 V and Fe(acac)$_3$ redox potential was -0.61 V. RRDE experiments were performed to calculate diffusion coefficient at both temperatures and found to decrease with the temperature drop. The electrochemical kinetic rate constant ($k_0$) of AcFc was found larger than Fe(acac)$_3$ but remains similar at both temperatures. NMR spectrum shows no difference in both temperatures for an anolyte and catholyte. Before and after battery experiments NMR data is the same which indicates the stability of both anolyte and catholyte. Overall battery performance at both temperatures was better than ARFBs.
ASSOCIATED CONTENT

Supporting Information Available: Battery Full cycles data, NMR

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Notes

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References


