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Increase of both solubility and working voltage by acetyl substitution on ferrocene for non-aqueous flow battery

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ABSTRACT

As a redox couple for flow batteries, the effects of acetyl group substitution on ferrocene (Fc) are examined on the aspect of solubility, oxidation potential, and chemical/electrochemical stability. The solubility of acetyl ferrocene (AcFc) (0.81 *M* at 25 °C) is 4 times larger than that for ferrocene (0.2 *M*) in a propylene carbonate-based electrolyte solution. This is rationalized by a decrease in solute/solute interactions and enhanced solute/solvent interactions resulting from acetyl substitution. The former can be explained by the reduction of molecular symmetry, which leads to a looser molecular packing in the solid state. The melting point, which is another barometer for solute/solute interactions, is also lower for AcFc. The enhanced solute/solvent interactions are due to the addition of a polar acetyl group, which enhances the polar interactions between the acetyl group and propylene carbonate solvent. Meanwhile, the oxidation potential moves to the positive direction (3.65 V *vs.* Li/Li$^+$ for AcFc and 3.44 V for Fc), which must be due to the introduction of an electron-withdrawing acetyl group. The acetyl ferrocene/acetyl ferrocenium couples are chemically/electrochemically stable at 3.3–4.1 V (*vs.* Li/Li$^+$). Due to this stability, a Li/AcFc coin-type non-flowing cell shows a reasonably good cycleability and Coulombic efficiency of >98%.

1. Introduction

Energy storage systems (ESSs) are considered a part of the infrastructures for future power management, in which a large amount of electrical energy should be stored particularly from intermittent renewable sources such as wind [1–5]. For this application, redox-flow batteries (RFBs) are considered as one of the promising energy storage devices. The most beneficial feature of RFBs is the easy control of capacity and power output, which is possible because the cell stack and electrolyte tanks are separated from each other. The capacity is determined by the size of the electrolyte tank and concentration of redox couples that are dissolved in the electrolyte. The power output is determined by the electrode area (current) and the number of cell stacks connected in series (voltage). RFBs have additional advantageous features over other candidates such as lithium-ion cells. Namely, as electric energy is stored/released into/from RFBs by electrochemical oxidation/reduction of redox couples on inert electrodes, electrode degradation is insignificant offering high longevity. This feature is contrasted by lithium-ion cells, in which the electrode material participates in the redox reaction becoming vulnerable to degradation.

The intrinsic drawback for this large-scale rechargeable battery is the lower energy density than that for lithium-ion cells. In particular, when aqueous electrolytes are used, both cell voltage and capacity are limited to give a limited energy density. The cell voltage limitation is due to water electrolysis and the capacity limitation results from the limited solubility of redox couples in aqueous electrolytes. The constraints relevant to cell voltage can be open by replacing the aqueous electrolytes with non-aqueous ones; for instance, those based on the organic carbonate solvents that are commonly used in lithium-ion cells. The carbonate-based non-aqueous electrolytes have a wider electrochemical stability window than aqueous ones, thereby the cell voltage can be enlarged above 1.23 V. Several redox couples have been proposed for non-aqueous RFBs; metal–organic frameworks, organic molecules and semi-solid systems [6–16]. The common feature for these redox couples is their poor solubility (commonly <0.1 *M*) in non-aqueous electrolytes, which should be solved to take advantage of non-aqueous RFBs [17].

Ferrocene (Fc) has been proposed as a promising redox couple due to its high chemical and electrochemical stability in non-aqueous electrolytes [18]. The one-electron oxidation to ferrocenium (Fc$^+$) and the reverse reaction are electrochemically reversible to be used as a reference electrode in non-aqueous electrolytes. The critical problem associated with this organometallic compound is, however, the poor solubility in non-aqueous electrolytes (0.04–0.2 *M* at ambient temperature) and somewhat low oxidation potential (3.44 V *vs.* Li/Li$^+$) as the positive redox couple for non-aqueous RFBs [16,19–22]. In order to solve or at least mitigate these two problems, in this work, one of the

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hydrogen atoms on the cyclopentadienyl ligands is replaced by an acetyl group. Two features are expected from the acetyl substitution. First, the molecular packing in solid-state becomes looser to reduce the intermolecular interactions. Hence, a solubility enhancement is expected. Second, the oxidation potential becomes more positive since the highest occupied molecular orbital (HOMO) level decreases due to the electron-withdrawing effect of the acetyl group.

In order for any redox couples to be applicable in flow batteries, other requirements should also be satisfied. One of the additional requirements is the chemical/electrochemical stability of redox couples, which has effects on the capacity retention and longevity of RFBs. The primary objective of this work was to examine how the acetyl group substitution on ferrocene has effects on the solubility, oxidation potential, and chemical/electrochemical stability.

2. Experimental

The room-temperature (25 °C) solubility was compared for ferrocene (Fc, Sigma Aldrich, 98%) and acetylferrocene (AcFc, Sigma Aldrich, 95%). To this end, 0.003 mol of Fc or AcFc was dissolved into 1.0 mL of 1.0 *M* $LiPF_6$ in propylene carbonate (PC). After stirring for 30 min at 25 °C, the undissolved residue was filtered off by a syringe filter (WHATMAN, 25 mm, 1 μm) and the Fe content in the filtrates was analyzed by using inductively-coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 4300DV, Perkin-Elmer). Differential scanning calorimetry (DSC, TA Instrument, UK) was used to determine the melting points of Fc and AcFc. The temperature ramp was 10 $°C\ min^{-1}$.

Cyclic voltammetry was employed to assess the oxidation potential and chemical/electrochemical stability of the two ferrocenes. To this end, 0.01 *M* of Fc or AcFc was dissolved into the electrolyte solution (1.0 *M* $LiPF_6$ in propylene carbonate (PC)). A glassy carbon electrode (area = 0.07 cm^2), silver wire and platinum flag were used as the working, reference and counter electrode, respectively. After the cyclic voltammetry, the Fc/Fc^+ redox couple (Sigma Aldrich, 98%) was added in the three-electrode cell to correct the reference electrode as the internal reference [18].

Galvanostatic charge/discharge cycling was performed by using a non-flowing type 2032 coin-cell, which comprises a Li foil/separator/cation-exchange membrane/carbon paper electrode in sequence [12]. The carbon paper (Toray, TGP-H-60) was pre-wetted with the electrolyte solution containing 0.5 *M* of AcFc. Before the cycling test, the separator (PP, Celgard®) and the cation-exchange membrane (Nafion 117®, Alfa Aesar) were soaked at least 12 h in the electrolyte solution.

3. Results and discussion

The solubility measurements reveal that AcFc is about 4 times more soluble in the non-aqueous electrolyte (1.0 *M* $LiPF_6$ in propylene carbonate) at 25 °C; 0.81 *M vs.* 0.20 *M* for Fc. The solubility enhancement by acetyl substitution can be explained by taking into account molecular interactions. In general, the solubility of a solute in a given solvent is decided by both the solute/solute interactions and solute–solvent interactions [26]. The rule of thumb predicts that the weaker solute/solute interactions and stronger solute–solvent interactions are desirable for high solubility. Here, another barometer for solute/solute interactions is the melting point of the given solute. That is, if the solute/solute interactions are weaker, the heat required for melting is lower, which appears as a lower melting point. Since the two parameters (solubility and melting point) are decided by solute/solute interactions, a strong correlation between the two can be assumed. A theoretical derivation in an ideal solution is given by: [24,25].

$$x_{\text{solute}} = e^{\left[-\frac{\Delta H_f}{R}\left(\frac{1}{T_{\text{solvent}}}-\frac{1}{T_{\text{m}}}\right)\right]}$$

Here, the x_{solute} is the mole fraction of a solute in a given solution (thus, solubility), ΔH_{f} is the enthalpy of fusion of the solute, T_{solvent} stands for the temperature for the solvent, and T_{m} is the melting point of the solute. This equation clearly reads that the lower values in both the melting point and enthalpy of fusion for solute molecules are desirable for high solubility. Meanwhile, Carnelley's empirical rule states that the molecules of a lower melting point have a lower packing density in the solid state and thus the solutes carry a less symmetric molecular shape [23]. Fig. 1 presents the differential scanning calorimetry (DSC) results obtained from Fc and AcFc. The enthalpy of fusion (ΔH_{f}) is comparable for two within an experimental error. However, there appears a significant decrease in the melting point by substituting the acetyl group in Fc. The melting points are 175 °C and 86 °C for Fc and AcFc, respectively. Surely, the molecules become less symmetric by introducing the acetyl group, which leads to looser molecular packing in the solid state and eventually lower melting behavior.

The solute–solvent interactions are another factor affecting solubility [27]. Here, '*the like dissolves the like*' rule states that polar solvents dissolve polar solutes. The high-polar and dielectric solvents are desirable for non-aqueous flow batteries because they should dissolve the salts such as lithium and alkylammonium salts [28]. In order for any redox couples to be dissolved into such polar solvents, they should also be polar with a high dielectric constant. In this work, the acetyl substitution converts the relatively non-polar ferrocene into the polar AcFc, thereby the solubility increases. In short, the 4-fold increase in solubility by acetyl substitution can be accounted for by the conversion into a less symmetric molecular shape (solute–solute interactions) and polarity increase (solute–solvent interactions).

The acetyl substitution offers another beneficial effect, which is the positive shift of oxidation potential. The redox potential of ferrocene ($E_{1/2} = 3.44$ V *vs.* Li/Li^+) is somewhat low as the positive redox couple. The acetyl group is an electron-withdrawing group, such that the highest occupied molecular orbital (HOMO) level will be lowered by acetyl substitution. If this is the case, the redox potential will move to the positive direction. This feature is clearly seen in Fig. 2a. The half-wave potential ($E_{1/2}$) is 0.2 V more positive for AcFc.

The chemical/electrochemical stability is another important requirement for the redox couples usable in RFBs. AcFc is chemically stable in non-aqueous electrolyte solutions. The electrochemical stability of the oxidized counterpart (acetyl ferrocenium, $AcFc^+$) is ensured from the absence of additional oxidation current up to 4.1 V (*vs.* Li/Li^+) (Fig. 2b). The chemical stability of $AcFc^+$ is examined by using cyclic voltammetry. Fig. 2b represents the cyclic voltammograms obtained in the 2nd and 50th scan. As is seen, two voltammograms are completely superimposed to each other without any additional current peaks and peak shift, manifesting itself that $AcFc^+$ is chemically stable in the given electrolyte solution. This feature is further ascertained from the scan-rate-dependent cathodic/anodic peak current ratio. If the $AcFc^+$ ions

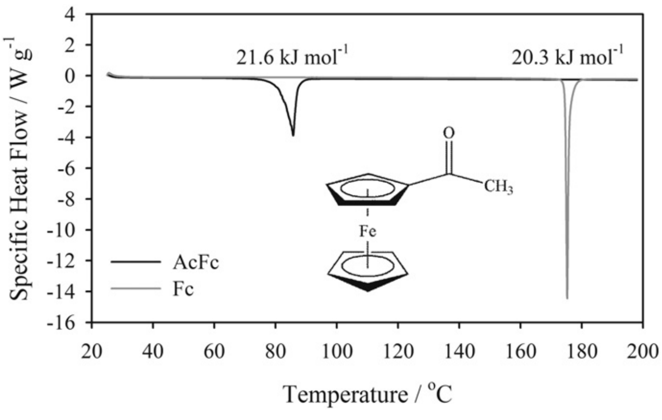

Fig. 1. Differential scanning calorimetry data obtained from AcFc and Fc.