



N-ferrocenylphthalimide; A single redox couple formed by attaching a ferrocene moiety to phthalimide for non-aqueous flow batteries

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HIGHLIGHTS

- A single redox couple, *N*-ferrocenylphthalimide is proposed by replacing H atom at the *N*-site of phthalimide with ferrocene.
- *N*-ferrocenylphthalimide was synthesized and has solubility of 0.3 M in background electrolyte.
- *N*-ferrocenylphthalimide exhibits increased stability in redox reactions of phthalimide while ferrocene moiety shows the stable redox reaction.
- Stability of *N*-ferrocenylphthalimide is implemented in cell test with an excellent CE of 97.3%.
- Fast kinetic of the proposed materials is verified by rate test with VE of 96.5–90.1%.

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ABSTRACT

N-ferrocenylphthalimide (FcPI) is prepared by replacing the hydrogen atom at the *N*-site of phthalimide with a ferrocene moiety. Phthalimide shows irreversible redox reaction due to H atom at the *N*-site of phthalimide. By replacing H atom of phthalimide with non-detachable functional group, such as alkyl group, redox reaction becomes reversible. Reversibility of redox reaction is requirement for redox couple due to cycling performance in battery system. In this work, electroactive group, not the simple functional group, is introduced to substitute H atom of phthalimide. As an electroactive group, ferrocenyl group has two main benefits. First, the redox reaction of the initial phthalimide with H atom at the *N*-site becomes reversible at $E_{1/2} = -1.87$ V (vs. Fc/Fc⁺) with an excellent stability. Second, FcPI is a single redox couple with $E_{\text{cell}} = 1.94$ V in a non-aqueous electrolyte because the ferrocene moiety in the molecule is also redox-active at $E_{1/2} = 0.07$ V (vs. Fc/Fc⁺) with stability. A non-flowing coin-type cell employing FcPI as a single redox couple exhibits an excellent Coulombic efficiency of 97.3% and stable cycle performance during the 50th cycle. Furthermore, rate test realizes fast charge transfer kinetics as voltage efficiency of 96.5–90.1% at 1.0–3.0 C.

1. Introduction

Redox flow batteries (RFBs) are rechargeable batteries offering a great promise for grid-scale and long-lifetime energy storage systems (ESSs). In RFBs, the redox couples dissolved in electrolytes are pumped into electrode compartments where an electrochemical reaction (charging) takes place on the inert electrodes. Then the charged redox couples are stored in external tanks. Discharging is performed by reversing these steps. The biggest advantage of RFBs over other rechargeable batteries is the decoupling of power and energy owing to the separation of electrochemical reactions (power) and storage (energy). The flexibility of the cell design makes RFBs well-suited to grid-scale energy storage devices [1,2]. Furthermore, the cell compartments except the

electrolytes are theoretically not prone to physical deformation because the electrochemical reactions take place on the surface of inert electrodes. And this sustaining compartments in the system leads to long-lifetime properties of RFBs.

However, the poor cycling performance associated with the cross-contamination is unavoidable. That is, conventional RFBs employ two different redox couples for the negative and positive redox reactions and therefore are called “dual redox couple systems.” Here, the two redox couples develop a difference in the concentrations of each redox couple across the separator. Therefore, the diffusion of the redox couples through the separator happens and this phenomenon is called cross-contamination. As a result, poor Coulombic efficiency, capacity loss, unwanted chemical reactions between the mixed redox couples,

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and shortening of cell life tend to occur [3–5].

Such undesirable consequences can be mitigated by using “single redox couple systems”. In single redox couple system, one molecule (a redox couple) is employed for both negative and positive electrochemical (charge/discharge) reactions [6–8]. In fact, cross-contamination is unavoidable, even in the single redox couple systems. That is, a redox couple is reduced and oxidized in the negative and positive electrodes respectively during cell charging. The reduced redox couple is enriched in the negative compartment, whereas the concentration of the oxidized redox couple increases in the positive compartment. A concentration difference arises for the charged redox couples (both reduced and oxidized redox couples) across the separator. The reduced redox couples moving from the negative compartment to the positive compartment by diffusion are oxidized in the positive compartment where they return to the initial discharged state. Similarly, the oxidized redox couple, after moving from the positive compartment to the negative compartment, is converted into the initial state through a similar pathway. The net result is the self-discharge of the cells and a loss of Coulombic efficiency because the reduced redox couple is oxidized in the positive side instead of being at the negative electrode during the discharging period, and vice-versa for the oxidized redox couple. Even if self-discharge is unavoidable for the single redox couple systems, the capacity loss can be avoided. It is because the charged species (both reduced and oxidized redox couples) can be collected in their initial discharged form which can participate electrochemical reaction on the other side. Note, however, that this condition arises only when the both of charged species are chemically stable in the electrolyte solutions.

Early research into RFBs focused on aqueous flow batteries that use water-soluble redox couples. However, there are several limitations on the aqueous redox couple systems. First, the water-based electrolytes are decomposed by electrolysis, which theoretically constrains the cell voltage to < 1.23 V. Second, some electrolytes are highly acidic and therefore cause corrosion of the electrodes and bipolar plates. Third, the working temperature is also restricted due to salt precipitation (e.g., vanadium redox flow cells) along with the thermodynamic properties (boiling point and freezing point) [9–11]. Non-aqueous flow batteries are on the rise as a counter-measure for aqueous flow batteries. In general, non-aqueous electrolytes are less corrosive and have a wider electrochemical stability window (esw) than aqueous types. Hence, the cell voltage of flow cells can be enlarged by using non-aqueous redox couples. Furthermore, non-aqueous electrolytes exhibit higher boiling points and lower freezing points than those of aqueous types. For example, acetonitrile frequently used as the solvent for non-aqueous redox couples has a lower freezing point (-44 °C) and moderate boiling point (82 °C) [12]. Furthermore, 1,3-dioxolane maintains its liquid phase between -95 and 78 °C [13–15]. This thermodynamic property makes non-aqueous RFBs more attractive ESSs for use in severe climates.

However, there is still a drawback for the non-aqueous redox couple systems. That is, non-aqueous redox couples tend to have low solubility in non-aqueous electrolytes (< 0.1 M) and slightly higher cell voltage than aqueous one. Therefore, prior research has focused on improving solubility and cell voltage of the redox couple with appropriate functional groups [16–19]. Additionally, only a handful of research is discussed regarding single redox couples working in non-aqueous flow batteries [20,21].

To that end, this work has started to improve the redox behavior of phthalimide (PI). Phthalimide is reduced by one-electron reaction at around -1.9 V (vs. Fc/Fc^+) (Fig. 2). However, the reverse oxidation current is not observed due to a chemical instability of the reduced species, resulting from a reaction between the reduced species (ketyl anion radical) and the hydrogen atom at the *N*-site of the phthalimide [22]. This irreversibility in redox reaction should be avoided to use organic molecule as a redox couple in redox flow batteries. That is, a reversibility of reaction leads to Coulombic efficiency and capacity retention in cell test. Chemical instability can be prevented by replacing

the hydrogen atom at the *N*-site of the phthalimide with non-detachable group, such as alkyl groups [22–24]. In the present study, the hydrogen atom at the *N*-site of the phthalimide is replaced by electroactive group, ferrocene (Fc), instead of alkyl group. Two benefits can be assumed by ferrocene substitution: (i) improvement of the chemical stability of reduced phthalimide (ketyl anion radical), and (ii) derivation of a possible single redox couple that is reduced at -1.9 V (vs. Fc/Fc^+) and oxidized at 0.0 V (vs. Fc/Fc^+) owing to additional redox reactivity from electroactive group. The use of ferrocene is justified because ferrocene shows a very stable redox behavior, to the point that it can be used as an internal reference [25]. The following objectives were identified in the present study: to test (i) whether the targeted molecules (ferrocene-substituted phthalimide, *N*-ferrocenylphthalimide (FcPI)) can be synthesized and exhibit a reasonable solubility in non-aqueous electrolytes, (ii) whether synthesized FcPI exhibits reversibility in the reduction of phthalimide moiety by attaching ferrocene group to phthalimide, (iii) whether FcPI exhibits overall two redox reactions (reduction and oxidation) within the electrochemical stability window of a non-aqueous electrolyte, (iv) whether the reduced (oxidized) species of FcPI are chemically stable, and (v) to obtain electrochemical performances (e.g., voltage efficiency, Coulombic efficiency, and rate properties) from non-flowing coin-cells, by which the viability of FcPI as a single redox couple can be verified.

2. Experimental section

Bromoferrocene, phthalimide, copper(I) oxide, and tetrabutylammonium tetrafluoroborate (TBABF_4) were purchased from Aldrich Chemical Co. *N*-ferrocenylphthalimide was prepared by the following method [26]. Specifically, bromoferrocene (0.53 g, 2 mmol), phthalimide (0.353 g, 2.4 mmol), and copper (I) oxide (0.172 g, 1.2 mmol) were mixed into 10 mL of 4-picoline and heated under reflux for 24 h in a nitrogen atmosphere. Then, 15 mL of dichloromethane was added, and the organic layer was filtered and washed with 5% sulfuric acid. The final product was obtained after filtration and drying overnight at 80 °C (yield = 60%). Proton nuclear magnetic resonance (^1H NMR) measurement was conducted using AVANCE III 500 spectrometers (500 MHz), and the sample was dissolved in deuterated chloroform (CDCl_3).

The solubility of the *N*-ferrocenylphthalimide was measured at a room temperature in an argon-filled glove box. A fixed amount of FcPI was placed in a flask, into which either the solvent (1,3-dioxolane) or the background electrolyte solution (1.0 M TBABF_4 in 1,3-dioxolane) was continuously added until the solid sample was completely dissolved. The maximal solubilities were determined from the total amount of injected solutions.

The redox behavior of the FcPI was examined by using cyclic voltammetry. To this end, 0.01 M of FcPI was dissolved in the background electrolyte (1.0 M TBABF_4 in 1,3-dioxolane). A glassy carbon electrode (with an area of 0.07 cm 2), a platinum plate, and a silver wire were used as the working, counter, and quasi-reference electrodes, respectively. The electrode potential was corrected by using ferrocene/ferrocenium (Fc/Fc^+) as the internal reference [25]. To investigate the chemical stability of the charged redox couples, two separate bulk electrolysis were performed by H-cell with a constant current of 53.6 μA and a 2.3 V voltage cut for reduction and oxidation. The electrolyte solutions collected from both sides of the H-cell were mixed and color change was monitored. Cyclic voltammogram was obtained after mixing then compared with voltammogram obtained before the charging. It is assumed that the two cyclic voltammograms are not completely superimposed if the charged redox couples are not chemically stable. That is, if they are chemically unstable, different cyclic voltammograms are obtained because they are converted to other chemical species. The H-cell was assembled by using two carbon-paper electrodes, electrolyte, and a pretreated separator membrane. The H^+ ions in the initial separator membrane (DuPont™; Nafion $^{\circledR}$ 117) were replaced by

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