



Electrochemical properties of a non-aqueous redox battery with all-organic redox couples



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ABSTRACT

A novel all-organic redox cell employing 4-Oxo 2,2,6,6-tetramethyl-1-piperidinyloxy (4-Oxo TEMPO) (as a catholyte) and (1S)-(+)-Camphorquinone (as an anolyte) is investigated through electrochemical measurements. From cyclic voltammetry tests, it is confirmed that electrochemically reversible redox processes of 4-Oxo TEMPO and (1S)-(+)-Camphorquinone occur at 0.48 V and -1.64 V (vs. Ag/Ag⁺), respectively. A non-aqueous redox battery with these redox couples can yield an estimated open circuit potential of 2.12 V at a 50% state of charge. The charge–discharge performance is assessed with an in-house designed non-flow single cell. Coulombic and energy efficiencies are 80.3% and 71.3%, respectively.

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1. Introduction

Redox flow batteries (RFBs) are a promising technology for large-scale energy storage systems (ESSs); these batteries utilize reduction and oxidation reactions of two active species in the electrolytes for charge and discharge processes [1]. With an external electrolyte reservoir containing redox couples, the flow batteries can independently scale the power and energy capacity components of the system [2–5]. Most RFBs are based on aqueous media containing redox couples such as iron/chromium [6], bromine/polysulfide [7], zinc/bromine [8], and all-vanadium [9,10] species. Huskinson's group [11] recently demonstrated that an aqueous flow battery based on the redox chemistry of 9,10-anthraquinone-2,7-disulphonic acid (AQDS) and a Br₂/Br[−] couple yields a peak galvanic power density exceeding 0.6 W cm^{−2} at 1.3 A cm^{−2}. The operating potential of such aqueous RFBs is limited by the electrochemical stability window of water, and hence low energy density is obtained.

Recently, non-aqueous RFBs have been receiving increasing interest because non-aqueous electrolytes offer the possibility of wider potential windows. Researchers have mainly focused on metal–ligand complexes as a redox couples in organic solvents [12–15]. Mun's group [15] demonstrated a non-aqueous redox system based on [Fe(bpy)₃(BF₄)₂] as the catholyte and [Ni(bpy)₃(BF₄)₂] as the anolyte in a propylene carbonate electrolyte. This system yielded an operating cell potential

of 2.2 V and the energy efficiency was found to be 81.8% at the first cycle. Li's group [16] studied a novel all-organic redox system based on 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the catholyte and N-Methylphthalimide as the anolyte in a non-aqueous NaClO₄/acetonitrile supporting electrolyte. The discharge plateau was observed at 1.36 V and the coulombic efficiency was about 90% in the first 20 cycles. Since the energy density of RFBs is determined by the cell potential and the total charge, these non-aqueous electrolytes with wide potential windows can offer higher energy density than aqueous electrolytes.

In this study, 4-Oxo TEMPO and (1S)-(+)-Camphorquinone were used as a catholyte and an anolyte, respectively. The large-scale utilization of flow batteries based on precious metals is limited by the relatively low abundance and high cost of these materials. Metal-free organic materials accordingly make it possible to decrease ESS cost compared to that of conventional RFBs.

2. Experimental

The catholyte and anolyte were prepared by dissolving 4-Oxo TEMPO (TCI) and (1S)-(+)-Camphorquinone (TCI) in a supporting electrolyte of 1.0 M TEABF₄/propylene carbonate (Panax Etech). With a 0.05 M solution of all-organic compounds (4-Oxo TEMPO and (1S)-(+)-Camphorquinone) and 1.0 M TEABF₄ in propylene carbonate, cyclic voltammetry was performed using an Autolab PGSTAT302N Potentiostat/Galvanostat (Ecochemie). Curves of current density versus potential were recorded for a three-electrode electrochemical cell with a Pt wire as the counter electrode, Ag/Ag⁺ as the reference electrode,

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and a freshly-polished 3 mm diameter glassy carbon as the working electrode.

The cell performance was determined using an in-house designed single non-flow cell. As can be seen in Fig. 1, the cell had a symmetric structure consisting of two copper current collectors, two graphite polar plates (Morgan Korea), two polypropylene frames, PVC gasket materials, two carbon felt electrodes (XF-30A, Toyobo) with an effective reaction area of 12 cm², and an anion exchange membrane (FAP-PP-375, FuMA-Tech). Catholyte and anolyte electrolytes were 0.2 M 4-Oxo TEMPO and 0.2 M (1S)-(+)-Camphorquinone in 1.0 M TEABF₄/propylene carbonate, respectively, and each electrolyte was supplied to the cell separately. Charge/discharge tests were conducted between 1.3 V and 2.6 V under a constant current mode at a current density of 1 mA cm⁻² at 30 °C using a battery cycler (Maccor 4000 Series).

3. Results and discussion

Fig. 2 shows cyclic voltammograms of 0.05 M 4-Oxo TEMPO (Fig. 2(a)) and 0.05 M (1S)-(+)-Camphorquinone (Fig. 2(b)) dissolved in the supporting electrolyte (1.0 M TEABF₄ in propylene carbonate) at the third scan. Fig. 2(a) shows that an electrochemically reversible redox process occurs at 0.48 V (vs. Ag/Ag⁺); this value is about 0.18 V higher than that (0.30 V) of TEMPO [16]. Functionalization of the TEMPO backbone with an electron-withdrawing group such as carbonyl is expected to yield a higher oxidation potential of 4-Oxo TEMPO, thereby raising the cell voltage. The peak separation of 4-Oxo TEMPO is 0.09 V at 10 mV s⁻¹. The narrow peak separation shows that the polarization of the electrode is very small, which indicates fast electrode reaction kinetics [17]. The ratio of the anodic peak current to the cathodic peak current is 0.99 at 10 mV s⁻¹, which means that the oxidized product of 4-Oxo TEMPO is stable over the timescale of the experiment at the given temperature. As can be seen in Fig. 3(a), in the anodic process of 4-Oxo TEMPO, the nitroxyl radical is oxidized to form a cation and joins the electrolyte anion to form oxoammonium salt; the reverse reaction occurs during the cathodic process [16]. Fig. 2(b) shows an electrochemically reversible redox process occurs at -1.64 V (vs. Ag/Ag⁺), and the peak separation is 0.09 V at 10 mV s⁻¹. The ratio of the anodic peak current to the cathodic peak current is 0.99 at 10 mV s⁻¹. Fig. 3(b) shows the redox reaction mechanism of (1S)-(+)-Camphorquinone.

The formal potentials for the reaction of 4-Oxo TEMPO and (1S)-(+)-Camphorquinone can be estimated by taking the average of the anodic and cathodic peak potentials. From the formal potentials of each half reaction, obtained in the cyclic voltammetry tests, it can be

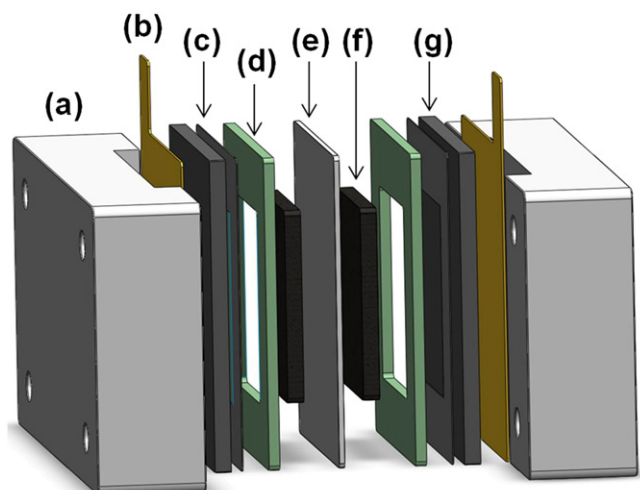


Fig. 1. Schematic diagram of a single non-flow cell: (a) endplate, (b) current collector, (c) gasket, (d) manifold, (e) membrane, (f) electrode, and (g) graphite plate.

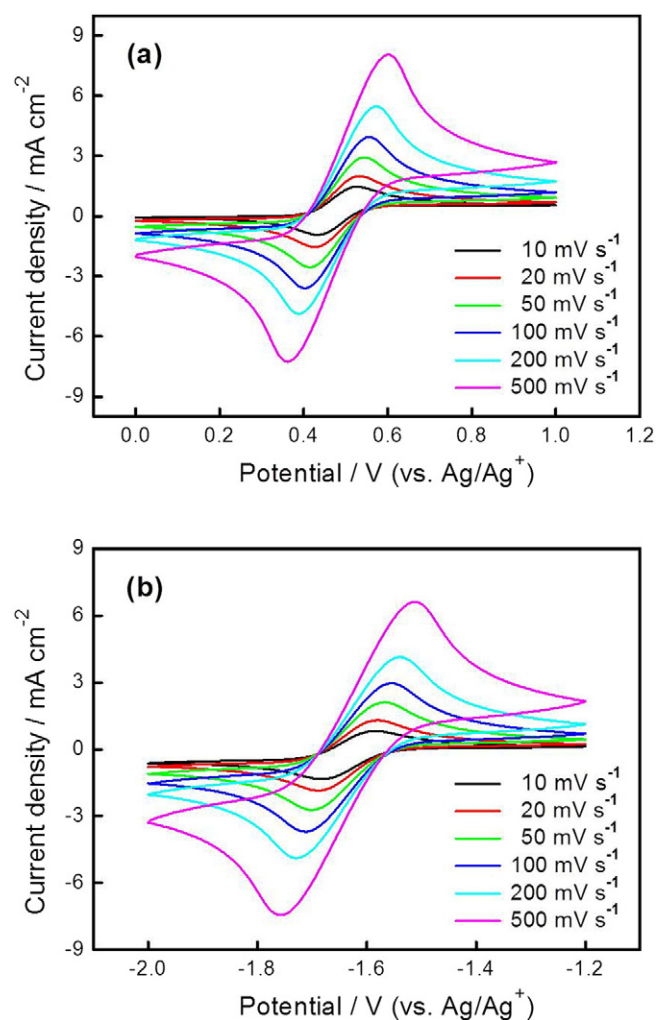


Fig. 2. Cyclic voltammograms measured on glassy carbons in (a) 0.05 M 4-Oxo TEMPO and (b) 0.05 M (1S)-(+)-Camphorquinone dissolved in 1.0 M TEABF₄/propylene carbonate.

concluded that a non-aqueous redox battery system can yield an estimated open circuit potential of 2.12 V at a 50% state of charge. This value is higher than the potential (1.60 V) of non-aqueous RFBs with all-organic redox couples (TEMPO as the catholyte and N-Methylphthalimide as the anolyte) [16].

Mass transfer properties can be estimated by plotting the peak current density based on the cathodic reaction versus the square root of the scan rate. As can be seen in Fig. 4, the peak current density values of the catholyte and the anolyte on glassy carbons are nearly proportional to the square root of the scan rate, implying that a diffusion process controls the redox reaction behavior of the all-organic redox couples. These observations indicate the presence of quasi-reversible electrode kinetics. The diffusion coefficients of the two redox species can be estimated using the Randles-Sevcik equations for electrochemically reversible and irreversible systems [18].

For reversible redox couple reactions, the peak current i_p is expressed by the following equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}.$$

For irreversible redox couple reactions, the equation changes to:

$$i_p = (2.99 \times 10^5) n^{3/2} \alpha^{1/2} A C D^{1/2} v^{1/2}.$$

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