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A chemically regenerative redox fuel cell using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl redox reaction in acid medium

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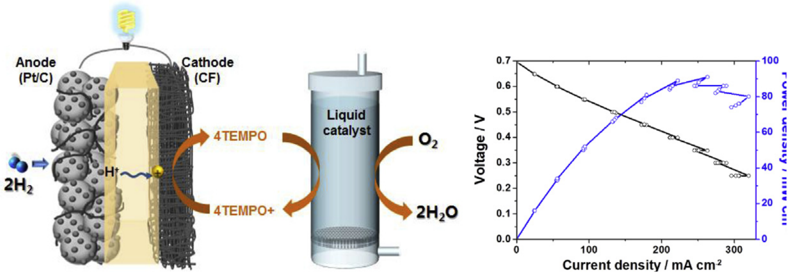
HIGHLIGHTS

- CRRFC was proposed using TEMPO instead of O_2 at the cathode.
- TEMPO showed fairly fast transport and low activation energy for the reduction.
- CRRFC exhibited an open circuit voltage of ~0.7 V at 30 °C.
- CRRFC exhibited a maximum power density of ~90 mW cm^{-2} at 30 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) with no free radical and non-volatile characteristic can be utilized as a liquid catalyst instead of O_2 at the cathode in a chemical regenerative redox fuel cell with H_2 as a fuel at the anode. In this study, the electrochemical properties and performance of TEMPO dissolved in sulfuric acid solution are investigated using half and unit cells. In the half-cell, TEMPO shows an activation energy of 1.27 kcal mol^{-1} K^{-1} for the reduction. A chemical regenerative redox fuel cell (CRRFC) using TEMPO as the liquid catalyst exhibits an open circuit voltage of 0.7 V and a maximum power density of 90 mW cm^{-2} at 30 °C with a low activation loss. The regeneration cycling test of the CRRFC is performed at a constant voltage of 0.4 V under a flow rate of the oxygen-bubbled TEMPO solution. The performance of the CRRFC deteriorates, i.e., a power density of zero measured at > 200 min. Thus, a highly efficient regeneration system needs to be developed for a high-performance CRRFC using TEMPO used as a liquid-type oxidant. Furthermore, stable liquid oxidants with relatively high standard reduction potentials can be proposed through various organic compounds.

1. Introduction

(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) with a chemical formula of $(CH_2)_3(CMe_2)_2NO$ is a chemical compound with a fairly stable radical, as proposed by Lebedev and Kazarnowskii in 1960's [1]. It has been used as mediators for radical maker, organic synthesis, and radical polymerization [2–5]. For example, TEMPO as an anode catalyst can be used to oxidize alcohol to aldehyde or aldehyde to carboxyl and can be continuously regenerated via the reoxidation process of the reduced TEMPO by oxygen [6–10], with no byproduct formation. Recently, it has been used in electrochemical reactions, involving ionic species and electrons as well as organic chemical process. Janoschka and Wang et al. reported a redox flow battery using TEMPO-based catholyte as an energy storage device with high-energy density and

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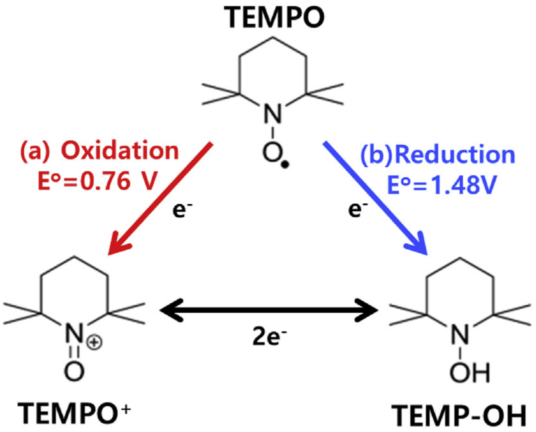

Fig. 1. The disproportionation and redox potential of TEMPO.

high efficiency [11,12].

A chemical regenerative redox fuel cell (CRRFC) is an alternative of polymer electrolyte membrane fuel cells (PEMFCs) used as solid-state non-precious metal catalysts for oxygen reduction reaction (ORR) [13–16]. The precious metals for cathode catalysts in PEMFCs have been mainly utilized because of their electrocatalytic activity for oxygen, stability in acidic media, and high electrical conductivity [17–22]. Instead of the solid-state metal catalysts for ORR, liquid catalysts such as TEMPO might be applied to the CRRFC with the redox reaction of the liquid catalysts. Thus, the reduced liquid catalysts at the cathode in the CRRFC can be chemically re-oxidized or regenerated by O_2 gas [22]. In the previous study, several liquid catalysts have been proposed for high-performance CRRFCs [23–25]. Herein, TEMPO with no free radical and non-volatile characteristic was firstly utilized as the liquid catalyst instead of O_2 at the cathode in the CRRFC with H_2 as the fuel at the anode.

In particular, TEMPO with a standard reduction potential of ~0.76 V (Fig. 1(a)) dissolved in 1 M H_2SO_4 was used as a liquid-type oxidant at the cathode [26–29]. TEMPO used as the liquid catalyst in CRRFC can be chemically oxidized to $TEMPO^+$ by O_2 (Eq. (1)). The oxidation reaction of TEMPO is also known as the regeneration reaction for $TEMPO^+$ as a liquid catalyst [30,31]. The oxidized liquid catalyst ($TEMPO^+$) acting as an oxidant, supplied at the cathode instead of O_2, can be electrochemically reduced to TEMPO on carbon felt electrode, consuming electrons (Eq. (2)). Furthermore, H_2 supplied at the anode in the CRRFC can be electrochemically oxidized (Eq. (3)). The overall reaction in the CRRFC with the oxidation of H_2 as a fuel at the anode and a reduction of TEMPO as a liquid catalyst at the cathode together with the regeneration reaction of Eq. (1) can be expressed by Eq. (4).

$$O_2 + 4TEMPO + 4H^+ \rightarrow 4TEMPO^+ + 2H_2O \tag{1}$$

$$4TEMPO^+ + 4e^- + 4H^+ \rightarrow 4TEMPO + 4H^+ \tag{2}$$

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{3}$$

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Electric energy} \tag{4}$$

2. Experimental

2.1. Synthesis of N-doped carbon felt (NCF)

The nitrogen-doped carbon felt electrode used as the cathode was prepared by heating a carbon felt with a volume of $2.24 \times 2.24 \times 0.65\ cm^3$ (SQ 10001, CeTech Co. Ltd) under an NH_3 atmosphere at 700 °C for 3 h.

2.2. Electrochemical reduction reaction of TEMPO in an acid medium

The electrochemical reduction reaction of TEMPO was characterized in a three-electrode electrochemical cell. A glassy carbon (GC), Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. Linear sweep voltammograms (LSVs) of TEMPO were obtained using a GC rotating disk electrode (RDE) with varying rotating speeds in N_2-saturated 1 M H_2SO_4 + 0.1 M TEMPO at 25 °C. The electrochemical reduction properties of TEMPO were characterized using a GC electrode in N_2-saturated 1 M H_2SO_4 + 0.1 M TEMPO at different reaction temperatures (30, 40, 50, and 60 °C).

2.3. Unit cell measurement

The membrane-electrode-assembly (MEA) for the CRRFC using TEMPO was fabricated by hot-pressing Nafion® 212 and Pt/C (0.1 $mg_{Pt}cm^{-2}$, E-TEK) with an area of 5 cm^2 as an anode at 110 °C under a pressure of 50 bar for 2 min. The as-prepared NCF electrode was used as the cathode. A monopolar plate with a serpentine channel was utilized for the anode whereas the plate with a plate-shape (3 mm in depth) was used as the cathode. The unit cell measurement for the CRRFC with the fabricated MEA was performed using a computer-controlled fuel cell station (CNL Energy, Korea) at 30 °C. Hydrogen gas with a relative humidity of 100% at 30 °C, was supplied at the anode at a flow rate of 30 mL min^{-1}. At the cathode, the 100 mL solution containing 0.3 M TEMPO and 1 M H_2SO_4 was supplied under a flow rate of 2 mL min^{-1}. The stability test of the CRRFC was performed at a constant voltage of 0.4 V for 200 min.

3. Results and discussion

Fig. 2 shows a schematic illustration of a CRRFC using TEMPO chemically oxidized by O_2 ($TEMPO^+$) as the liquid catalyst (denoted as CRRFC-TEMPO). At the anode in the CRRFC-TEMPO, H_2 as the fuel is electrochemically oxidized on a Pt/C catalyst (Eq. (3); namely "Hydrogen Oxidation Reaction (HOR)" with the same structure as that of typical proton exchange membrane fuel cells (PEMFCs) using O_2 as an oxidant supplied at the cathode. The proton (H^+) and electron produced by the HOR at the anode transport to the cathode and are electrochemically reduced with $TEMPO^+$ as a liquid catalyst at a reduction potential of 0.76 V (Eq. (2)). The theoretical cell potential of the CRRFC-TEMPO, the difference between the HOR (0 V) and the reduction of TEMPO (0.76 V), by the total electrochemical reaction (Eq. (4)) is 0.76 V.

The electrochemical properties of TEMPO in an acid medium, the CV and LSVs were investigated by cyclic voltammetry (CV) and LSV on a GC in N_2-saturated 0.1 M TEMPO + 1 M H_2SO_4 (Fig. 3). The

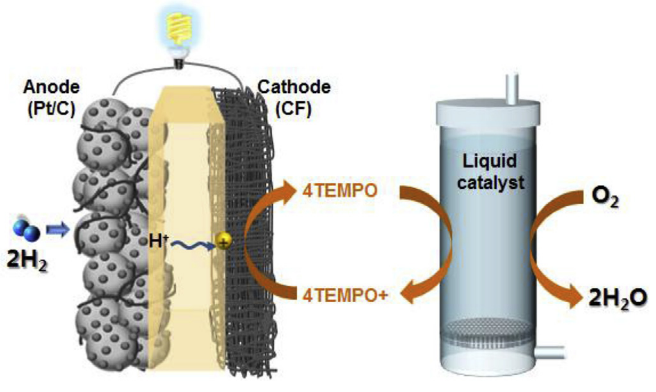

Fig. 2. A schematic illustration of the CRRFC operated using $TEMPO^+$ as the liquid catalyst at the cathode connected with a chemical regeneration system by O_2 and H_2 as the fuel at the anode.