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Short communication

# Designing current collector/composite electrode interfacial structure of organic radical battery

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ABSTRACT

Charge/discharge processes of organic radical batteries based on the radical polymer's redox reaction should be largely influenced by the structure and the composition of the composite electrodes. AC impedance measurement of the composite electrodes reveals a strong correlation between the overall electron transfer resistance of the composite electrode and the material of the current collector, and suggests that the electric conduction to the current collector through the contact resistance should be crucial. We also find that the adhesion and the contact area between the composite electrode and the current collector strongly influence the contact resistance rather than the work functions and the volume resistivities of the composite electrode and the current collector. It is also confirmed that the charge/discharge performance of the composite electrode is related to the overall electron transfer resistance of the composite electrode. These results indicate that the charge/discharge performance of the radical battery is dominated by the interfacial electron transfer processes at the current collector/carbon fiber interface. In fact, the composite electrode which has a high adhesion to the current collector shows a small overall electron transfer resistance and an excellent charge/discharge performance. The rate performance would be much improved by suitably designing the interfacial structure including adhesion and contact area.

## 1. Introduction

Recently, organic polymers with redox-active and chemically stable radical pendant substituents are attracting much attention due to its specific characteristics based on their rapid and repeatable oxidation/reduction capabilities [1–6]. The typical example of the pendant substituents in the so-called radical polymers is the 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO) groups, which is sufficiently robust as well as rapidly, reversibly, and stoichiometrically oxidized to the corresponding oxoammonium cation via chemical or electrochemical oxidation. Studies on the redox chemistry of the radical polymers have been encouraged by our recent approach to the "radical battery" [7–15], which is characterized by an excellent rate performance and potential capability of fabricating purely organic, paper-like, and flexible rechargeable energy-storage devices. A schematic of the radical battery structure and the mechanism of charge/discharge processes of the battery are shown in Scheme 1. Radical batteries are featured by the use of the radical polymers as the cathode-active materials, together with anode-active materials such as Li metal sandwiching an electrolyte layer. The typical cathode consists of the radical polymer, a carbon fiber as the conductive additive, and a small amount of binders to enhance adhesion to current collectors. The charge/discharge processes of the batteries are based on the radical polymer's redox reaction. The carbon fibers work as the electric conduction path to assist the repeatable oxidation/reduction processes throughout the radical polymer layer. The structure and composition of the radical polymer/carbon fiber composite electrode are thus one of the most important factors and determine the overall characteristics of the radical battery. We supposed that determination of the factor, most responsible for the overall electron transfer reactions, is the shortcut to improve the battery performance. In this paper, we report the electrochemical analysis on the radical polymer/carbon fiber composite electrodes with a view to unravel the most influential factor for the overall charge/discharge process, focusing on the electron transfer resistance [16–18] obtained from impedance spectroscopy. We demonstrate that the charge/discharge properties of the composite electrode are dramatically improved by modifying the interfacial structure that is one of the most important factors. These results provide a design principle to fabricate radical batteries with excellent performances.

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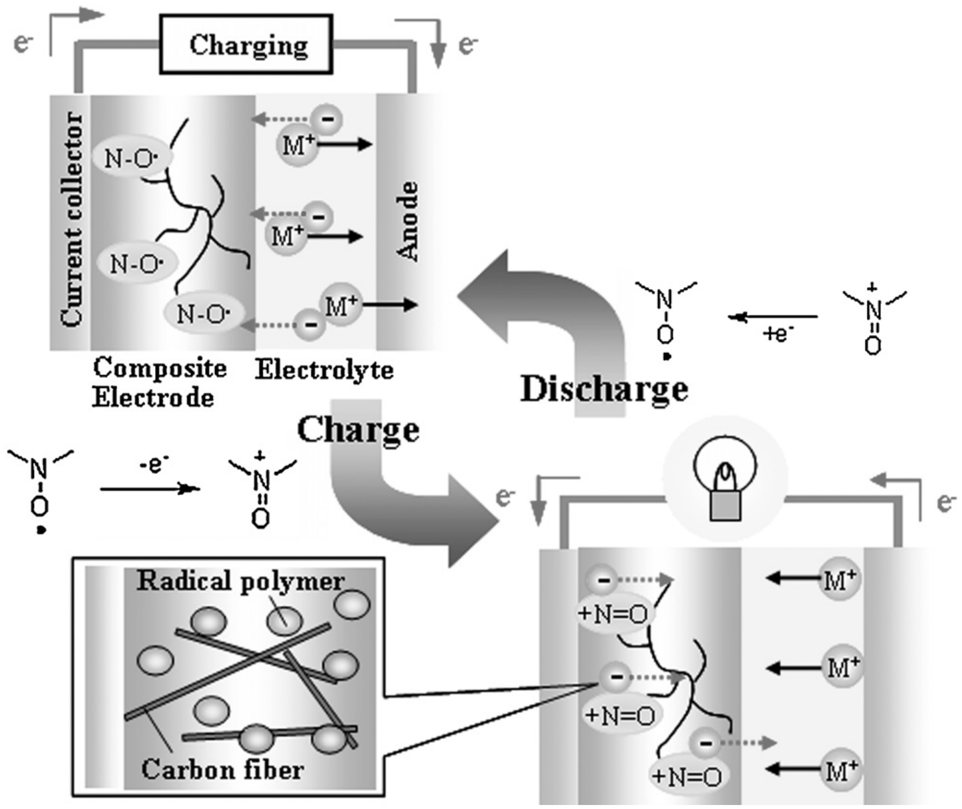

**Scheme 1.** Charge/discharge mechanism of the radical battery.

## 2. Experimental

### 2.1. Materials

All solvents were purchased from Kishida Kagaku Co. Poly(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl vinyl ether) (PTVE), the radical polymer employed as the electrode-active material in this report, was prepared as described previously by our group [19–21]. A vapor-grown carbon nanofiber (VGCF-H) was purchased from Shouwa Denko Co. Poly(vinylidene fluoride) (PVdF) resin (KF#1300), employed as a binder resin in an *N*-methyl-2-pyrrolidone (NMP) based ink (i.e. a dispersion of the polymer/carbon nanofiber), was purchased from Kureha Chemical Co. An electrochemical grade solution of 1 M lithium bis(pentafluoroethanesulfonyl)imide (LiBETI) in propylene carbonate (PC) was purchased from Kishida Kagaku Co. All materials were used without further purification.

### 2.2. Preparation of composite electrodes

The radical polymer/carbon fiber composite electrodes were prepared on current collectors using several kinds of inks by stencil printing process. We prepared several compositions of NMP-based inks for our experiment. The preparative method for the composite electrodes from the NMP-based inks was as follows. A radical polymer, PTVE, was mixed with VGCF-H and PVdF in NMP by a relatively low-powered disperser to obtain the NMP-based inks. Nonvolatile content of each NMP-based ink was adjusted to 10%. The obtained inks were stencil printed with a contact metal mask to give wet films with thickness around 180 μm on various substrates (i.e. current collectors such as an ITO/glass plate, a platinum plate, and a glassy carbon plate), and then dried under vacuum at 80 °C for 12 h to give several kinds of the composite electrodes of the same size ($A = 1\ \text{cm}^2$) and thickness (about 20 μm) with varied composition, PTVE/VGCF-H/PVdF = 10/80/10, 30/60/10, 50/40/10, and 70/20/10 (w/w/w). Hereinafter NMP-based inks with compositions of PTVE/VGCF-H/PVdF = 10/80/10, 30/60/10, 50/40/10, and 70/20/10 (w/w/w) are abbreviated as N1, N2, N3, and N4, respectively. Thicker films of the composite electrodes were obtained similarly by using the corresponding thicker metal masks. A SEM image of a composite electrode was obtained without any deposition using a 3D real surface view microscope (VE-9800/Keyence Co.). The SEM image of the composite electrode prepared from N1 (Fig. 1) showed a typical network of the carbon fibers and the radical polymer was situated within the carbon network. The carbon fiber network provide a conducting path which allows the repeatable redox processes of the radical polymer, and the redox efficiency of

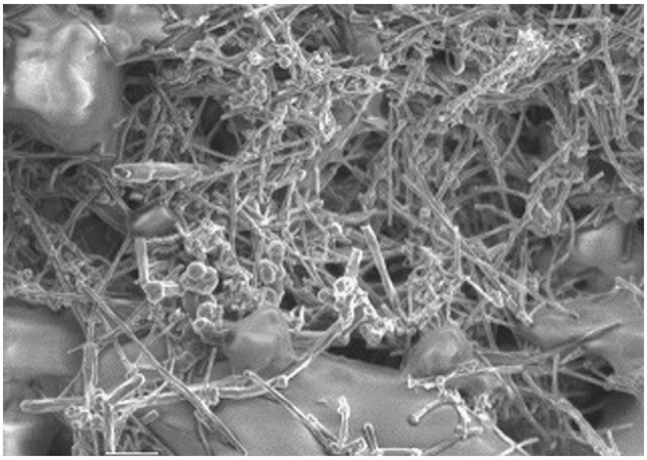

**Fig. 1.** SEM image (5000×) of the composite electrode prepared from N1. The fibrous network corresponds to the carbon fiber, and the clayey particle corresponds to the radical polymer.