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Effects of the Addition of Calcium on the Pseudocapacitance of Ruthenium Oxide Electrodes

Yoshio TAKASU,* Takeshi OHNUMA, Syunsuke MIZUTANI, Wataru SUGIMOTO, and Yasushi MURAKAMI

Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University (3-15-1 Tokida, Ueda 386-8567, Japan)

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The electrochemical properties of Ru-Ca-O_x/Ti electrodes prepared by a dip-coating method were evaluated. A Ru (40%)-Ca(60%)-O_x/Ti electrode exhibited high pseudocapacitance of 143 mC cm⁻² in an alkaline electrolyte which was 20 times larger than that of RuO₂/Ti. This value was equivalent to 638 F g⁻¹ for the RuO₂ loaded on the electrode. The present electrodes have a potential for use as electrochemical capacitors.

Key Words : Electrochemical Capacitor, Ruthenium Oxide, Calcium Oxide, Pseudocapacitance

1 Introduction

Electrochemical capacitors are candidates as high-power density energy-storage devices for vehicles and other electric devices.¹⁾ Ruthenium-based oxide materials have been widely studied owing to their high energy density, high electrical conductivity, rapid reversibility, and chemical stability.²⁻⁴⁾ Since ruthenium oxide is expensive and scarce, various approaches have been attempted to minimize the amount of ruthenium in the oxide phase and to obtain higher energy density (charge per mass of RuO₂).⁵⁻⁹⁾ We have reported that the pseudocapacitance of dip-coated ruthenium oxide electrodes can be enlarged by the addition of transition elements such as Mo, V, or La, *etc.*^{5, 6, 8-11)} We report here on the improvement in the pseudocapacitive behavior of ruthenium based electrodes by the addition of calcium which is light and inexpensive.

2 Experimental

Oxide-coated electrodes in this investigation were prepared by a conventional dip-coating method. Commercial titanium rods (1.6 mm in diameter, 99.5%) were used as the substrate. These rods were etched in 10% oxalic acid solution at 80°C for one hour, washed, and then dried in air. Ethylene glycol solutions of RuCl₃·*n*H₂O and Ca(NO₃)₂ was mixed in the required molar ratios. The nominal molar ratios of Ru : Ca will be presented in brackets throughout this paper. Titanium rods were dipped into the solution and pulled up at a rate of 1 mm s⁻¹. The dipped electrodes were dried at 60°C and calcined at 450°C in a preheated furnace in air for 10 minutes. The dip-coating process was repeated 10 times.

A beaker-type electrochemical cell equipped with the working electrode, a platinum mesh counter electrode, and a Ag/AgCl reference electrode was used for electrochemical measurements. A Luggin capillary faced the working electrode at a distance of 2 mm. The electrolyte

was 1.0 M NaOH or 0.5 M H₂SO₄. The cyclic voltammograms of the electrodes were recorded after a stabilization procedure of the electrodes, typically 200 potential sweep cycles at 500 mV s⁻¹ in the electrolyte. The pseudocapacitance of the electrode per geometric surface area, *q*, was calculated from cyclic voltammograms between 0.1-0.9 V (*vs.* RHE) in NaOH or 0.3-1.1 V (*vs.* RHE) in H₂SO₄ at a scan rate of 50 mV s⁻¹.

The surface morphology of the electrodes were observed with a high-resolution field emission-scanning electron microscope (FE-SEM). The roughness factor (RF) of the electrodes before and after 200 potential sweep cycles were measured by the xenon gas adsorption method with an ultra-high vacuum system. X-ray diffraction (XRD) was utilized for structural analysis.

3 Results and Discussion

Figure 1 shows typical steady-state cyclic voltammo-

Fig. 1 Steady-state cyclic voltammograms of (a) RuO₂/Ti, (b) Ru(50%)-Ca(50%)-O_x/Ti and (c) Ru(40%)-Ca(60%)-O_x/Ti electrodes in 1 M NaOH at 50 mV s⁻¹.

Fig. 2 The relationship between the nominal ruthenium content and the pseudocapacitance per geometric surface area for Ru-Ca-O_x/Ti electrodes.

grams of the RuO₂/Ti and Ru-Ca-O_x/Ti electrodes. By the addition of calcium, a clear increase in the pseudocapacitance was observed. The relationship between the ruthenium content and voltammetric charge density, q , is shown in Fig. 2. A maximum value of 143 mC cm⁻² (255 F g⁻¹) was achieved for the Ru(40%)-Ca(60%)-O_x/Ti electrode, which is roughly 20 times larger than that of RuO₂/Ti (6.7 mC cm⁻²). Moreover, this value is equivalent to 638 F g⁻¹ for the loaded amount of RuO₂.

XRD revealed that RuO₂ and CaO were present in the as-prepared electrodes as crystalline phases. The surface morphology of the electrodes is shown in Fig. 3. No clear change in the surface morphology was observed in the alkaline electrolyte, even after 200 potential sweep cycles. The roughness factor, RF, of Ru(40%)-Ca(60%)-O_x/Ti after the electrochemical measurement was RF = 64 which corresponds to a 1.5 times increase compared to RF = 40 for RuO₂/Ti. Since the pseudocapacitance was enlarged by 20 times by the addition of calcium, the enhancement in the electrochemical property can not be due solely to this increase in the roughness. In order to understand the structure of this electrode more clearly, electrochemical measurements were conducted in an acidic electrolyte to dissolve the Ca species. Figure 3(c) shows the FE-SEM image of the Ru(40%)-Ca(60%)-O_x/Ti electrode after electrochemical measurement in 0.5 M H₂SO₄, revealing a porous RuO₂ network. Therefore it is suggested that RuO₂ was highly dispersed within the Ca species, resulting in an improvement in the utilization of electrochemically active RuO₂.

Despite the porous texture of Ru-Ca-O_x/Ti in an acidic electrolyte, the effect of the addition of calcium on the increase in pseudocapacitance was less-greater than that in the alkaline electrolyte; the electrode (Ru(40%)-Ca(60%)-O_x/Ti) exhibited only 89 mC cm⁻². This is most likely due to the stripping off of the active material, RuO₂, due to the decrease in mechanical strength when the Ca

Fig. 3 FE-SEM images of Ru(40%)-Ca(60%)-O_x/Ti electrodes: (a) before electrochemical measurement and after 200 potential sweep cycles in (b) 1.0 M NaOH and (c) 0.5 M H₂SO₄.

species was leached out into the acidic electrolyte.

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