Dip-Coated Ru-Mo-O/Ti Electrodes for Electrochemical Capacitors

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RuO_2-MoO_3/Ti electrodes prepared by a dip-coating method provide an extremely large pseudocapacitance showing that they have a potential for use as electrochemical capacitors. The highest pseudocapacitance was 208 F g^{-1} for RuO_2(50)-MoO_3(50)/Ti. The voltammetric charge of this electrode, 166 C g^{-1} between 0.3 and 1.1 V (*vs.* RHE), corresponds to 0.48 protons contributed to the adsorption and desorption on every loaded ruthenium, if the probable contribution of molybdenum to the pseudocapacitance was neglected.

Although RuO_2-based oxide-coated titanium electrodes have been used for various electrolytic processes, they also have a potential for use as electrodes for elctrochemical capacitors due to their large pseudocapacitance.[1,2] Ruthenium is an expensive material; therefore, various approaches have attempted to use a minimum amount of ruthenium for the capacitors; for instance, (1) dispersion of RuO_2 over less expensive oxides having large surface areas,[3] (2) preparation of ultrafine ruthenium oxide particles by sol-gel methods,[4,5] (3) alloying of ruthenium oxide with other oxides,[6] (4) preparation of porous RuO_2 layer with help of rare earth elements,[7] or (5) search for non-expensive materials such as NiO,[8] nitrides,[9,10] of V, Nb, Mo, and W. In the present investigation, the authors have found that MoO_3 is an effective supporting material for the high dispersion of RuO_2.

Oxide-coated electrodes in the present investigation were prepared by a dip-coating method. Commercial 99.5% titanium rods, 1.6 mm in diameter, were used as the substrates. The $RuCl_3$ solution (50 mg [Ru] ml^{-1}) in ethylene glycol was mixed with the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution (50 mg [Mo] ml^{-1}) in ethylene glycol + 25% aqueous ammonia (1:1) in the required ratios. The titanium substrates etched in 10% oxalic acid solution at 80 °C for one hour were dipped into the solutions. The dipped electrodes were dried at 60 °C for 10 min and calcined at 450 °C in a preheated furnace for 10 min. The process of dip-coating, drying, and calcination was repeated 10 times. The oxide loading was estimated at about 0.7 mg cm^{-2} for all the electrodes used in this experiment from the weight increase by coating. The beaker-type electrochemical cell equipped with a working electrode, a platinum plate counter electrode, and a Ag/AgCl reference electrode was used. The geometric surface area of the working electrode was 1 cm^2. A Luggin capillary faced the working electrode at a distance of 2 mm.

Figure 1 shows the steady-state cyclic voltammograms of RuO_2/Ti, MoO_3/Ti and various compositions of the RuO_2-MoO_x/Ti oxide electrodes in 0.5 M (1 M = 1 mol dm^{-3}) H_2SO_4. The redox peaks are observed around 0.63, 0.78 and 1.28 V for the RuO_2/Ti electrode above 0.3 V, while they are observed between 0.63 - 0.69 V for the MoO_3/Ti and the RuO_2-MoO_x/Ti binary electrodes. The voltammetric charge density between 0.3 ~ 1.1 V (*vs*. RHE) , q^*, reached a maximum value of 116 mC cm^{-2} (or 166 C g^{-1}, 208 F g^{-1}) at the RuO_2(50)-MoO_x(50)/Ti electrode, which is about 40 times as large as that of the RuO_2/Ti

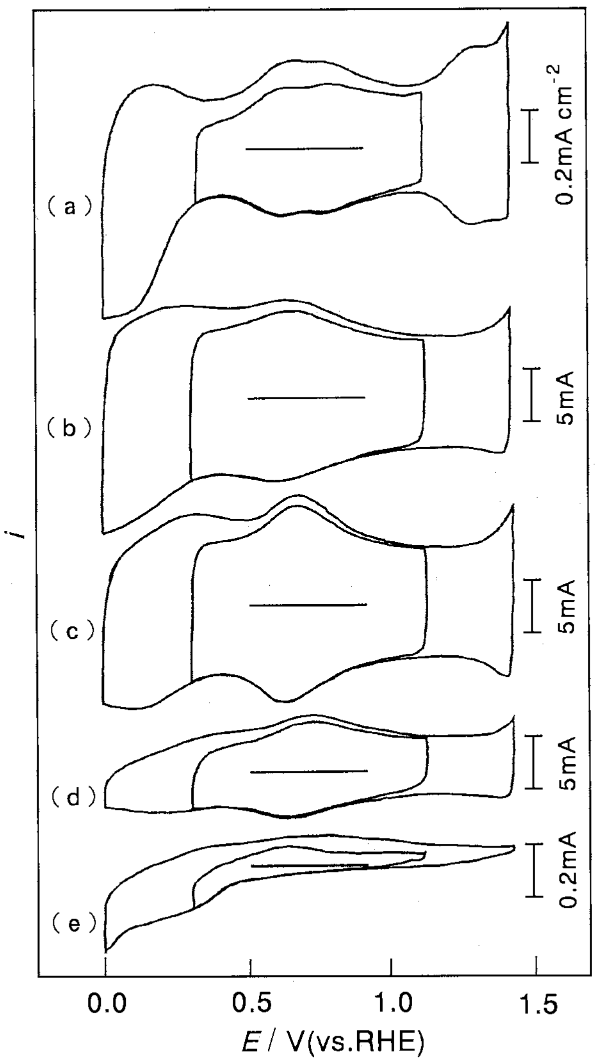

Figure 1. Steady-state cyclic voltammograms of various compositions of dip-coated RuO_2-MoO_x/Ti electrodes. Electrodes: (a) RuO_2(100)/Ti, (b) RuO_2(70)-MoO_x(30)/Ti, (c) RuO_2(50)-MoO_x(50)/Ti, (d) RuO_2(30)-MoO_x(70)/Ti, (e) MoO_x(100)/Ti. Electrolyte: 0.5 M H_2SO_4. Potential sweep rate: 50 mV s^{-1}.

electrode. The q^* value of 166 C g^{-1} for the electrode means that η_{Ru} is 0.48 in the potential range, where η_{Ru} is defined as the number of protons which contribute to the adsorption/desorption on every loaded ruthenium assuming that the following reaction proceeds as the charge/discharge reaction for the RuO_2-base oxide

$$RuO_2 + H_2O + H^+ + e^- \rightleftarrows Ru(OH)_3$$

electrodes. When the potential sweep range was expanded to 0 and 1.4 V (see Figure 1 c), η_{Ru} increased to 0.87, suggesting

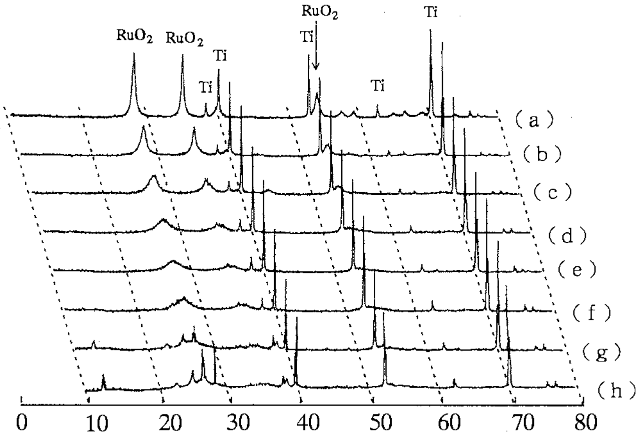

Figure 2. XRD patterns of various compositions of dip-coated RuO_2-MoO_x/Ti electrodes. Electrodes: (a) RuO_2(100)/Ti, (b) RuO_2(70)-MoO_x(30)/Ti, (c) RuO_2(50)-MoO_x(50)/Ti, (d) RuO_2(30)-MoO_x(70)/Ti, (e) MoO_x(100)/Ti. X-ray: CuKα.

that ruthenium oxide was almost completely dispersed over the molybdenum oxide or it formed a $Ru_xMo_yO_z$ compound.

Figure 2 shows the X-ray diffraction patterns for the RuO_2/Ti, MoO_3/Ti and various compositions of the RuO_2-MoO_x/Ti binary oxide. With an increase in the molybdenum content, the diffraction peaks of the rutile-type RuO_2 became broad with no change in the diffraction angle, and traces of the diffraction peaks of MoO_3 appeared at RuO_2(50)-MoO_x(50). This means that RuO_2 was more finely dispersed over the amorphous molybdenum oxide with the molybdenum content; however, it was dispersed over the molybdenum oxide-containing crystal MoO_3 beyond RuO_2(50)-MoO_x(50)/Ti. Since the MoO_3/Ti electrode also showed a pseudo-catacitive property and the redox peaks of the RuO_2-MoO_3/Ti electrodes appeared at different potentials from those of the RuO_2/Ti electrode as shown in Figure 1, it is probable that the molybdenum oxide can also contribute to the large pseudo-capacitance of this binary oxide electrode system by helping the electroconductive ruthenium oxide.

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