Extremely High Pseudo-Capacitance of RuO_2 Highly Dispersed on Glassy Carbon

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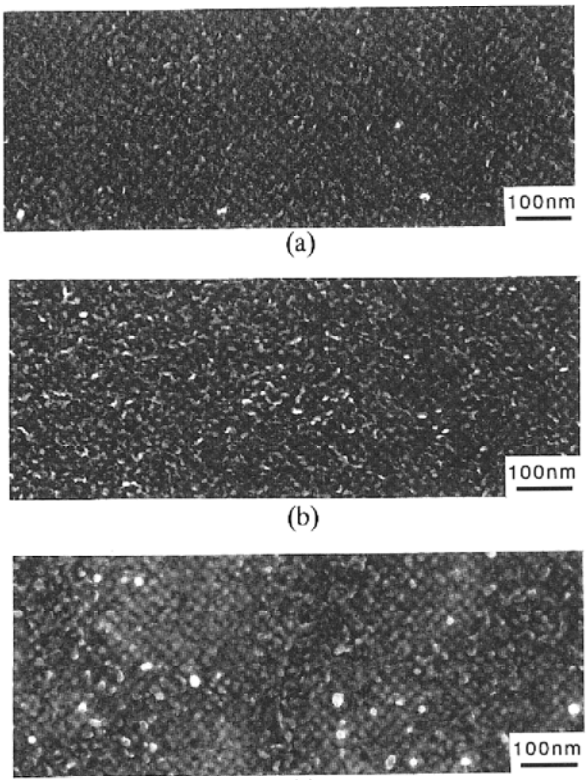
By means of a model electrode method, it has been found that the ruthenium oxide highly dispersed on glassy carbon produces an extremely large surface charge density which corresponds to more than one proton adsorbs on every ruthenium loaded on the glassy carbon, if the charge was supposed to be caused only by the adsorption of proton on the RuO_2.

The RuO_2-based electrodes for the electrochemical capacitors can have a higher energy density than porous carbon electrodes.[1-4] Since ruthenium is an expensive material, it is generally required that ruthenium species must be finely dispersed over either a less expensive oxide having large surface area[2-4] or an electro-conducting porous material such as carbon.[5,6] If a metal oxide can be finely and tightly dispersed on electroconducting carbons, it can be a candidate for the oxide electrode of electrochemical capacitors, where it has the ability for the adsorption/desorption of protons on it. Therefore, a basic evaluation is expected concerning the clarification of the interaction of metal oxides with carbon materials.



(a)

(b)

(c)

Figure 1. High-resolution SEM images of a GC and two RuO_2/GC electrodes. Electrodes: (a) GC, (b) and (c) RuO_2/GC. The amount of RuO_2 loaded: (b) 2.5 nmol cm^{-2}, (c) 125 nmol cm^{-2}.

In the present investigation, we used ruthenium oxide as an example of the oxide material showing a pseudo-capacitive property, and applied a model electrode method using a polished surface of a GC (glassy carbon) as the supporting material.[7] Although some pseudo-capacitive properties of ruthenium oxide supported on porous carbon materials have been reported,[5,6] no quantitative information has yet so far been presented.

A GC rod (Tokai Carbon Co., Ltd., GC-20S; 6 mm diam., 3 cm length) was used as the substrate. The GC was buff-polished with an alumina suspension (60 nm diam.) prior to use. The 1-butanol solutions of various $RuCl_3$ concentrations were dropped onto the GC surface with a micro-pipette. It was dried at 60 °C for 10 min and calcined in air at 400 °C in a preheated furnace for 20 min. The amount of ruthenium loading was controlled either by the concentration of the $RuCl_3$-butanol solution or by the amount of the solution added. The beaker-type electrochemical cell equipped with a working electrode, a platinum gauze counter electrode, and a Ag/AgCl reference electrode was used. A Luggin capillary faced the working electrode at a distance of 2 mm.

Figure 1 shows the high-resolution SEM images of a polished GC and two RuO_2/GC (2.5 nmol-RuO_2/cm^2, and 125 nmol-RuO_2/cm^2) electrodes. The formation of the rutile-type RuO_2 was confirmed by an XRD measurement. Although the ruthenium oxide formed particles on the GC surface, no drastic aggregation seems to occur on the GC, probably due to the existence of many defects on it.

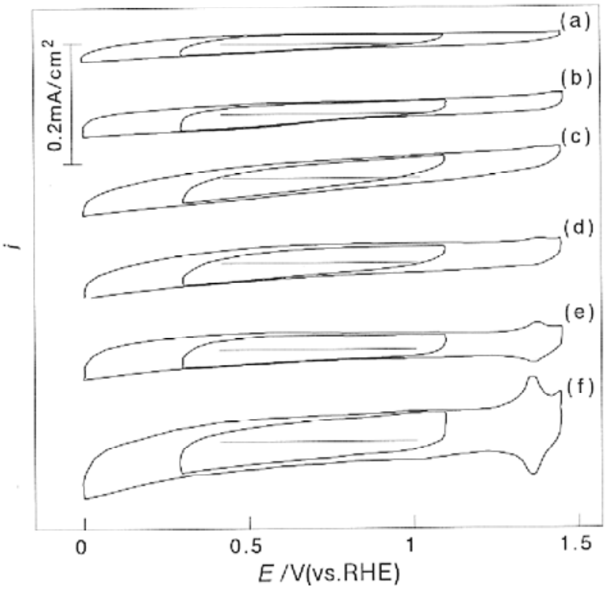


Figure 2. Steady-state cyclic voltammograms of GC and RuO_2/GC electrodes in 1 M KOH at 50 mV s^{-1}. The amount of RuO_2 loaded: (a) GC (0 mol cm^{-2}), (b) 0.50 nmol cm^{-2}, (c) 1.0 nmol cm^{-2}, (d) 5.0 nmol cm^{-2}, (e) 10 nmol cm^{-2}, (f) 50 nmol cm^{-2}.

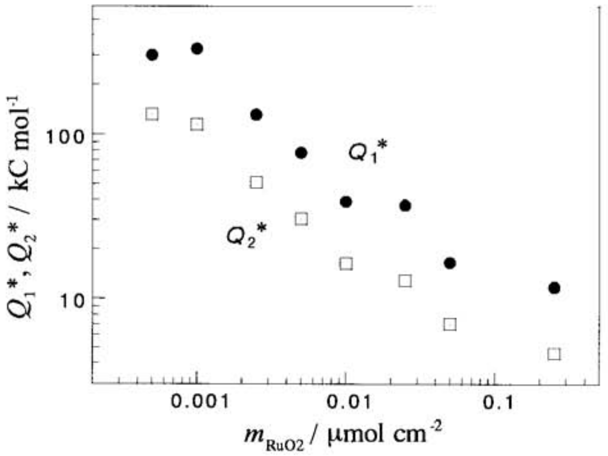


Figure 3. The charge per unit amount of RuO_2 for the RuO_2/GC electrodes, Q_1^* and Q_2^*, determined by cyclic voltammetry in the potential range of 0.3 - 1.1 V (*vs*. RHE) and 0.0 - 1.45 V (*vs*. RHE) in 1 M KOH at 50 mV s^{-1}. m_{RuO2} means the amount of RuO_2 loaded on 1 cm^2 of GC.

In Figure 2, the steady-state cyclic voltammograms of the GC and the RuO_2/GC electrodes loaded with various amounts of RuO_2 are presented. The voltammetric charges, the half values of the respective sum of the cathodic and anodic voltammetric charges, between 0.0 - 1.45 V (*vs*. RHE) and 0.3 - 1.1 V (*vs*. RHE) are named q_1^* and q_2^*, respectively. The surface charge density per unit amount of RuO_2, Q^*, is defined by $Q^* = (q^* - q_{\mathrm{GC}}^*)/m_{\mathrm{Ru}}$, where q_{GC}^* and m_{Ru} mean the voltammetric charge of the GC electrode and the amount of RuO_2 loaded on 1 cm^2 of GC, respectively. As shown in Figure 3, Q_1^* and Q_2^* for each of the RuO_2/GC electrodes increase with a decrease in the amount of RuO_2-loading. The Q_2^* does not absolutely include the amount of charge due to the evolution of hydrogen and/or oxygen; while Q_1^* might include a small amount of such charges. At 96.5 kC mol^{-1}, η_{Ru} is unity, where η_{Ru} is defined as the number of protons which contribute to the adsorption/desorption on every loaded ruthenium. The cathodic voltammetric charge for these electrodes must then caused by the adsorption of the proton on the oxide and the charge of the electric double layer of the surfaces of both the RuO_2 and the exposed area of the GC. It is noteworthy that the Q_1^* and Q_2^* values exceed 96.5 kC mol^{-1} for the electrode loadings less than 25 nmol cm^{-2} and 1.0 nmol cm^{-2} of RuO_2, respectively. Although the precise evaluation of the net charge due to the adsorption of proton is difficult, both the Q_1^* value of 329 kC mol^{-1} and the Q_2^* value of 132 kC mol^{-1} seem to be extremely large. The former and the latter values correspond to about 3.4 and 1.4 protons contributing to the charge of the electrode, respectively, if the charges were supposed to be caused only by the adsorption of proton on the RuO_2. These values are significantly higher than the values so far reported concerning the amount of protons adsorbed on the RuO_2-based electrodes.[1-4]

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