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Surface Microstructure of Oxide-Coated Electrodes for Chlorine Evolution

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Synopsis. By use of high-resolution scanning electron microscopy and electron probe X-ray microanalysis, the surface structure of RuO_2–IrO_2-TiO_2/Ti electrodes has been clarified. It is composed of highly grown Ti-deficient crystallites and ultrafine Ti-rich oxide particles of 5—20 nm in diameter, forming a porous structure.

The oxide-coated titanium anode generally used in chlor-alkali industries is composed of a mixed oxide of RuO_2, IrO_2 and TiO_2. This kind of electrode, called DSA®, which is generally prepared by thermal decomposition of metal chloride and alkoxide after painting their alcoholic solution onto titanium substrate, is not only catalytically active for chlorine evolution but also highly stable under the evolution of chlorine and oxygen.[1)] A variety of microanalyses have established that both the surface morphology and the composition of this type of electrodes are heterogeneous.[1—11)] The resolution of the electron microscopy adopted so far, however, has not been sufficient to discuss the porosity of the electrodes. In order to elucidate the structure of active sites of these electrocatalysts and to develop further applications, we must clarify the precise morphology and composition of their surface layers. In particular, the reason why DSAs® have large surface areas has not yet been clarified. Transmission electron microscopy can analyze the microstructure of porous materials, however, it cannot give decisive information of their surface structure.[8)] In the present investigation HR-SEM (high-resolution scanning microscopy) and EPMA (electron probe X-ray microanalysis) were adopted to reveal the surface microstructure of dip-coated RuO_2–IrO_2–TiO_2/Ti electrodes.

Experimental

The RuO_2–IrO_2–TiO_2/Ti electrodes were prepared by a conventional dip-coating method from titanium plate and *n*-butanol solutions of ruthenium(III) chloride, iridium(III) chloride, and titanium tetrabutoxide tetramer in required mol ratios. The preparation procedure of the electrodes and macroscopic surface compositions evaluated by cyclic voltammetry, temperature desorption spectrometry with CO adsorption and X-ray photoelectron spectroscopy were described in a previous paper.[9)] The overall compositions of this electrode system determined by EPMA using 25 keV incident electron beam was almost the same as the nominal compositions. The X-ray diffraction patterns of this system gave only rutile-type structure, with almost symmetric but rather broad peaks except for the sharp peaks of titanium substrate.[9)] Surface morphology of the electrodes were observed with a HR-SEM equipped with a field emission electron gun (Hitachi S-5000). The chemical analysis of the electrode surface was carried out by EPMA (JEOL JXA-8600MX; incident electron beam size of 1 μm in diameter with energy of 10 keV).

Results and Discussion

Figures 1 and 2 show scanning electron micrographs of typical regions of 60%RuO_2–20%IrO_2–20%TiO_2/Ti and 20%RuO_2–20%IrO_2–60%TiO_2/Ti electrodes. Many deposits are observed on the flat planes, a) in Fig. 1, and along the edge part of the cracks, a) in Fig. 2, of the electrodes. Micrographs in higher magnification of the deposits are presented in b) of Figs. 1 and 2. These deposits appear to be highly grown crystallites having characteristic planes of the rutile-type oxide.

More striking was the result that the apparently flat parts at lower magnification were clarified to be composed of ultrafine particles with sizes of ca. 5—20 nm in diameter, c) of Figs. 1 and 2. Their crystallinity seems to be low with no characteristic planes. These small particles condensed randomly with each other, giving micropores between the particles. The porosity of the flat part was higher for the Ru-rich oxide-coated electrode than that for the Ti-rich oxide-coated electrode. The formation of many cracks on the latter electrode must be related to the stress due to the relatively higher packing density of these ultrafine oxide particles. Up to now no authors have presented such porous microstructure, other than the cracks and deposited crystallites on the DSA electrodes. For example, Kodintsev and his coworkers have presented SEM micrographs of RuO_2–IrO_2/Ti electrodes with a magnification of ×10000, but, they have not observed the microporous structure of their flat parts.[10)].

To analyze the composition of the surface crystallites on these electrodes, EPMA was adopted, using a rather low energy incident electron beam, 10 keV. The penetration depth, mean free path, of the electrons having kinetic energy of 10 keV is about 20 atomic layers. An example of the EPMA images of ruthenium, iridium and titanium is presented in Figs. 3 and 4, with SEM micrographs of the same parts. Comparison of the secondary electron images of the electrodes with their EPMA images suggests that the highly grown crystallites on the Ru-rich oxide-coated electrode, Fig. 3, are composed of Ir-deficient RuO_2 oxide without titanium species, while

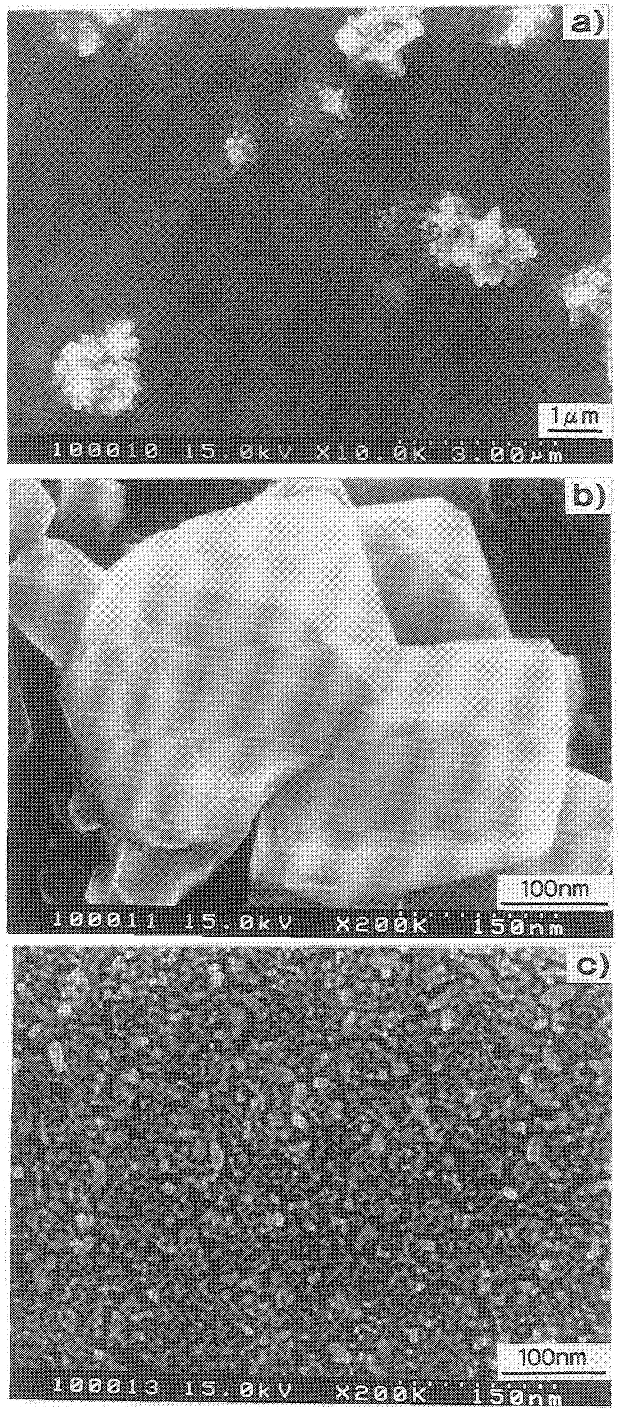

Fig. 1. High-resolution SEM micrographs of a $60\%RuO_2–20\%IrO_2–20\%TiO_2/Ti$ electrode. a): a typical part (×10000), b): crystallites on the electrode surface (×200000), c): a typical flat part (×200000).

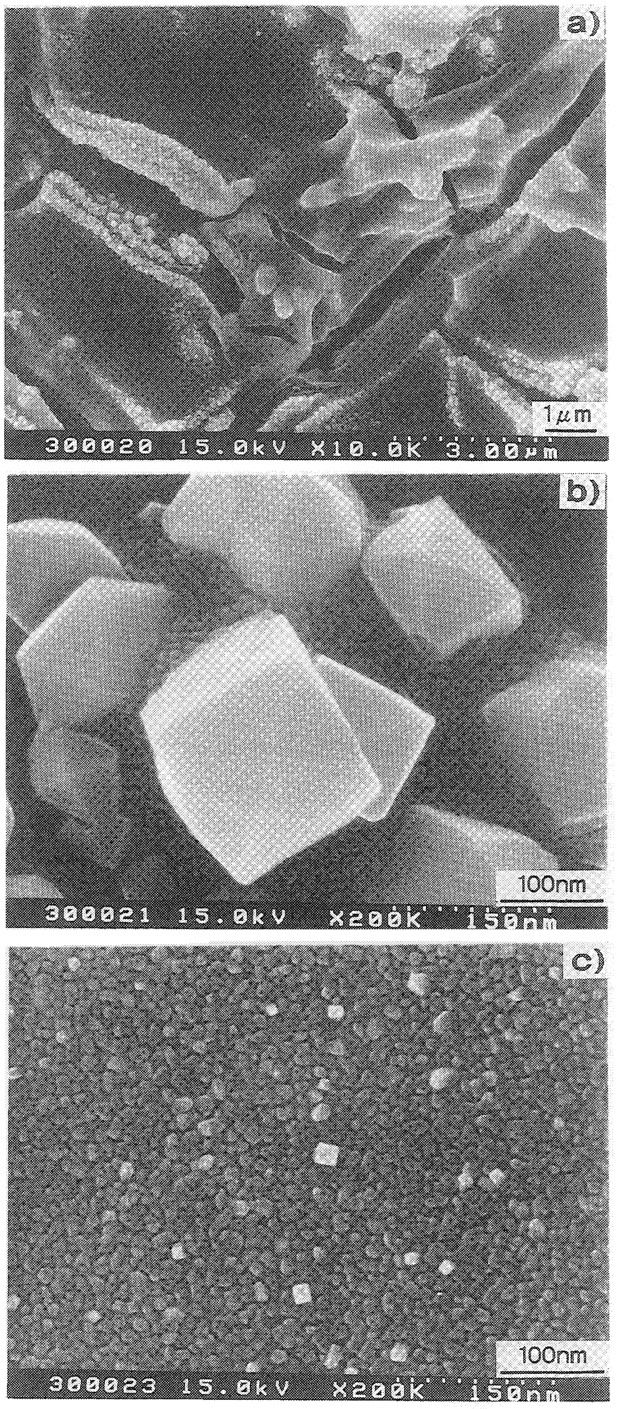

Fig. 2. High-resolution SEM micrographs of a $20\%RuO_2–20\%IrO_2–60\%TiO_2/Ti$ electrode. a): a typical part (×10000), b): crystallites along the crack part (×200000), c): a typical flat part (×200000).

the crystallites along the edge of the cracks on the Ti-rich oxide-coated electrode, Fig. 4, are composed of a mixed oxide of ruthenium and iridium. On the other hand, the flat part of the Ru-rich oxide electrode seems to be composed of a mixed oxide of iridium and titanium, while that of Ti-rich oxide electrode seems to be composed of a Ti-rich oxide with a low content of iridium.

As described above, the application of HR-SEM and EPMA with low energy incident electron beam has succeeded in clarifying the complicated microstructure and the composition of the heterogeneous surface of $RuO_2–IrO_2–TiO_2/Ti$ electrodes, DSAs. This information will

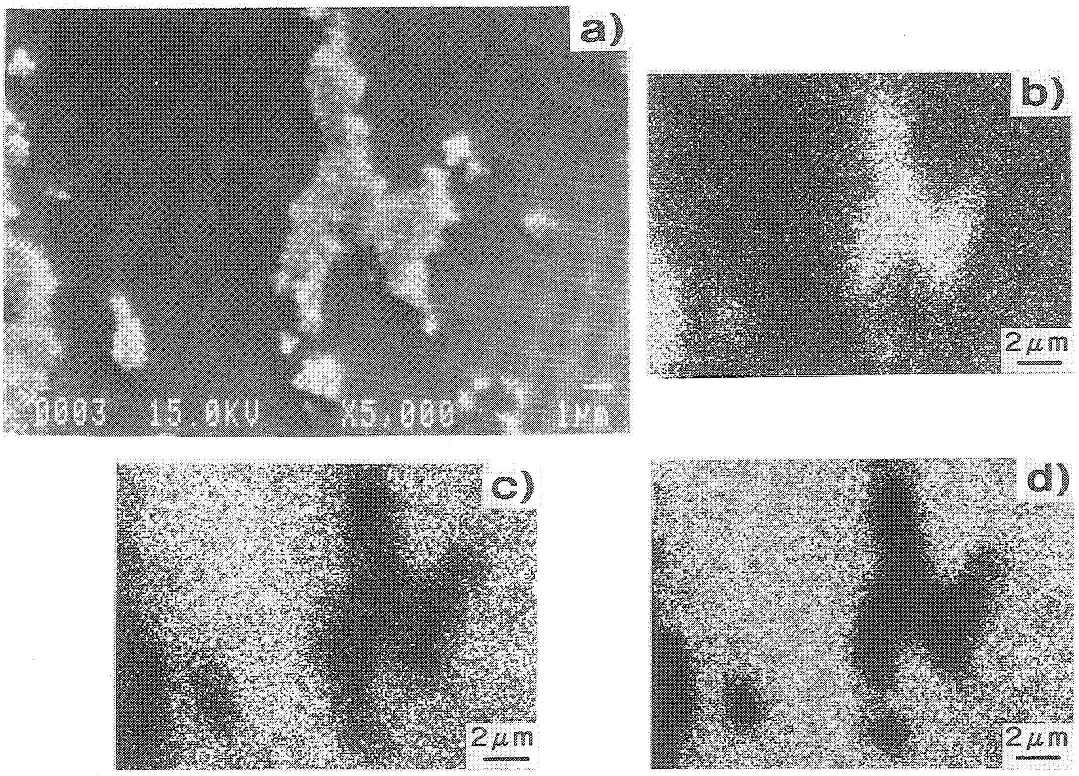

Fig. 3. A SEM micrograph and EPMA images of the same part for Ru, Ir, and Ti of 60%RuO_2–20%IrO_2–20%TiO_2/Ti electrode. a): SEM, b): EPMA image of Ru, C): EPMA image of Ir, d): EPMA image of Ti. Incident electron beam energy for the EPMA: 10 keV. Spot size of the electron beam for the EPMA: 1 μm in diameter. The maximum brightness of each element: Ru 144, Ir 233, Ti 93. The minimum brightness of each element: Ru 45, Ir 100, Ti 11.

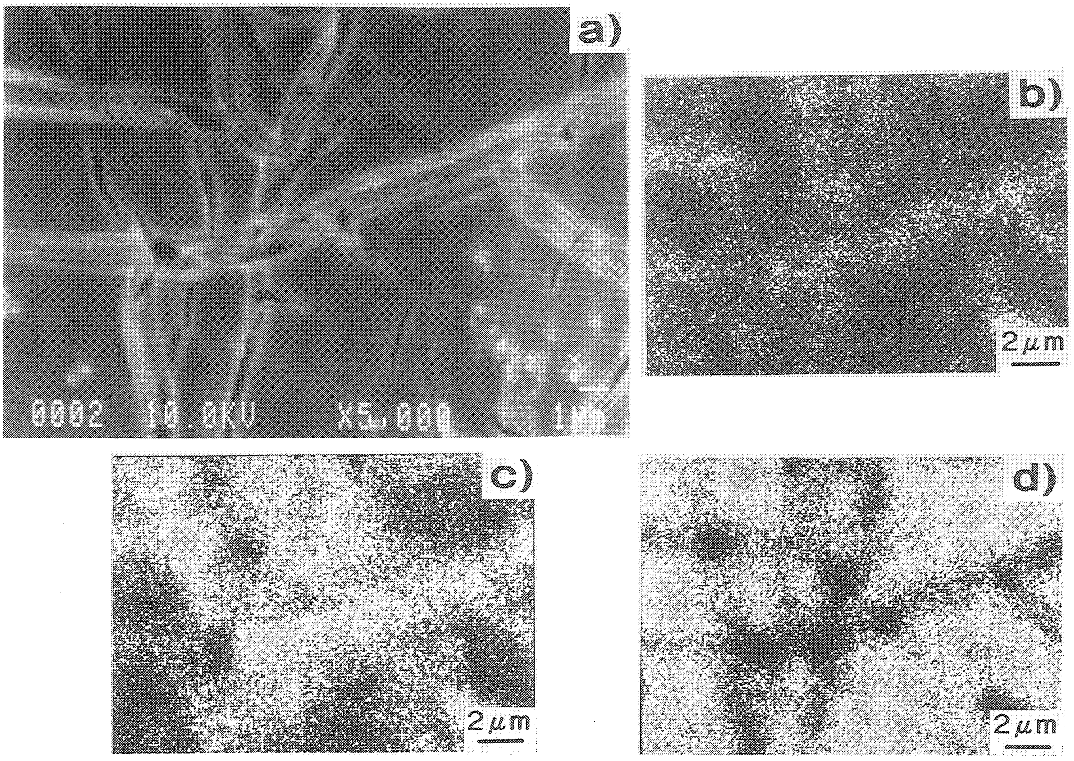

Fig. 4. A SEM micrograph and EPMA images of the same part for Ru, Ir, and Ti of 20%RuO_2–20%IrO_2–60%TiO_2/Ti electrode. a): SEM, b): EPMA image of Ru, C): EPMA image of Ir, d): EPMA image of Ti. Incident electron beam energy for the EPMA: 10 keV. Spot size of the electron beam for the EPMA: 1 μm in diameter. The maximum brightness of each element: Ru 58, Ir 229, Ti 209. The minimum brightness of each element: Ru 7, Ir 101, Ti 83.

be able to contribute both to understand the structure of the active sites of this electrode system and to design more active electrode. Quantitative analysis of the composition of highly grown oxide crystallites is important, however, such microscopic analysis is very difficult at present.

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