

## Characteristics of Ru and RuO<sub>2</sub> Thin Films on the Conductive Ceramics TiO and Ebonex(Ti<sub>4</sub>O<sub>7</sub>)

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Metallic oxide coatings have been studied and successfully developed in electrochemical technology to solve the limitations of metallic anodes such as high wear rate and a sharp occurrence of passivation phenomena.<sup>1-3</sup> Well known DSA (dimensionally stable anode) type electrodes are ruthenium dioxide and iridium dioxide on titanium, which are used by the chlor-alkali industry for chlorine evolution.<sup>4-7</sup> Metal oxide electrodes such as RuO<sub>2</sub> are commonly prepared by thermal decomposition of ruthenium metal salts, *i.e.*, RuCl<sub>3</sub> and Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, which are applied as thin coatings on a metallic substrate, usually titanium. Bulk ruthenium dioxide (RuO<sub>2</sub>) has metallic conductivity (about  $2 \times 10^4 \Omega^{-1} \text{cm}^{-1}$  at room temperature) and exhibits good electrocatalytic activity for oxygen evolution in both acid and alkaline electrolytes. Ruthenium metal is also a good electrocatalyst for oxygen evolution, even though it suffers from a lack of stability and corrodes badly during oxygen evolution.<sup>3</sup>

Titanium based materials already play an important role in electrochemistry because of their high conductivity or high stability. Among Ti-O system, TiO<sub>x</sub>,  $0 \leq x \leq 1.2$ , has metallic conductivity and also Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>5</sub>O<sub>9</sub> are known to have comparably high conductivity.<sup>8,9</sup> Recently, electrochemical applications of the conductive Magneli phase, Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>5</sub>O<sub>9</sub>, have been attracted much attention.<sup>10-12</sup> Ebonex, a conductive ceramic material mainly composed of the Magneli phase titanium oxides, Ti<sub>4</sub>O<sub>7</sub>, is considered as an electrode material, because its bulk conductivity matches that of carbon and graphite electrodes (resistivity; 630 (ohm·cm × 10<sup>-6</sup>) for Ti<sub>4</sub>O<sub>7</sub> and 1375 for carbon). It is resistant to corrosion in aqueous electrolytes and shows no tendency to form hydride in contact with hydrogen. Pollock *et al.*<sup>10</sup> reported high overpotentials for both hydrogen and oxygen evolution at Magneli phase titanium oxide electrodes. Pletcher *et al.*<sup>11</sup> demonstrated that kinetics of ferro/ferricyanide couple were slow at an Ebonex electrode. Also, they have electrodeposited five metals such as Cu, Au, Ni, Pd, and Pt on the Ebonex electrode and investigated electrochemical behavior of the electrodes and possible use of the electroplated Ebonex electrodes.<sup>12</sup>

TiO having metallic conductivity shows appreciable ranges of composition, TiO<sub>0.8</sub>-TiO<sub>1.2</sub>. TiO has an ordered defective NaCl-type structure in which one-sixth of the sites for each

type of ion are unoccupied.<sup>13,14</sup> Recently, platinum has been electrodeposited well onto TiO surfaces without substantial overpotentials. The electrochemical properties of the Pt deposited onto TiO are the same as the characteristics of a platinum electrode, which demonstrates that TiO can be one of the excellent substrates for electrodes.<sup>15</sup>

In this communication, we wish to report the electrochemical properties and morphologies of RuO<sub>2</sub> and Ru on the conductive ceramic TiO and Ebonex (Ti<sub>4</sub>O<sub>7</sub>). RuO<sub>2</sub> coatings are commonly prepared on a metallic substrate, *i.e.*, titanium, by thermal decomposition. It is found that RuO<sub>2</sub> layer can also be coated well on conductive metal oxides such as TiO and Ti<sub>4</sub>O<sub>7</sub>. In addition, Ru metal can be electrochemically deposited on Ti<sub>4</sub>O<sub>7</sub> and TiO.

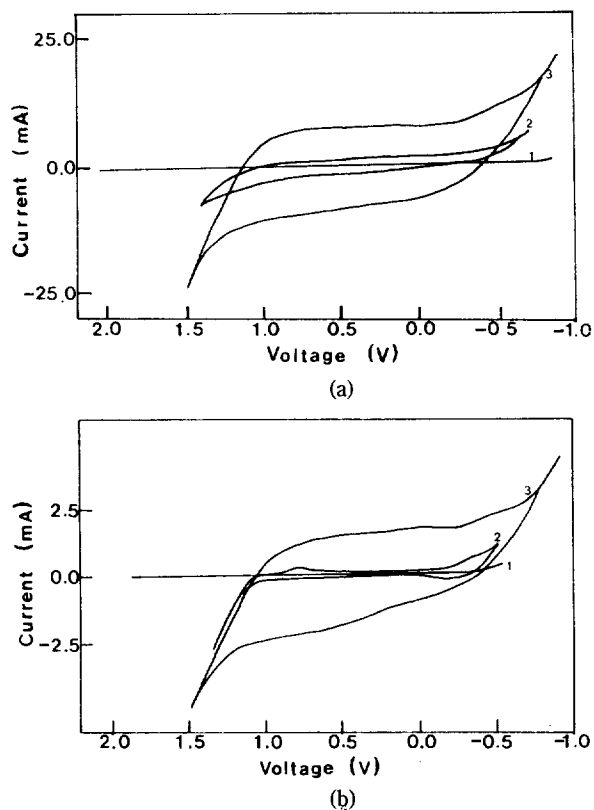
TiO was formed by arc melting of TiO<sub>2</sub> and Ti under Ar atmosphere. Ebonex ceramic electrodes were purchased from the Electrosynthesis Co. Ebonex rod (dia. 6.2 mm) was cut into a disk whose length was 4 mm. The electric contacts of the electrodes were made with silver paste to a copper wire, and the electrodes were encapsulated in glass tubes with epoxy. One face of the TiO granule or Ebonex disk was ground with sandpaper, polished with alumina (stepwisely 1.0, 0.3, and 0.05 μm), sonicated and washed thoroughly before use.

Ruthenium metal film was deposited electrochemically on polished TiO surfaces by applying -0.8 V for 30 minutes in the 10 mM RuCl<sub>3</sub> in 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution at 60 °C. For the Ebonex electrode, Ru was plated electrochemically at -1.4 V for one hour in the same solution, because Ru was not able to be plated onto the electrode surfaces at lower potentials. RuO<sub>2</sub> layer was prepared by the most common technique, *i.e.*, thermal decomposition of a metal salt. RuCl<sub>3</sub> was dissolved in 20% HCl and evaporated. The residue was dissolved again in a small amount of isopropanol and the resultant paste was applied to the electrode surface by brushing. The salt layer was dried and thermally decomposed at 380 °C for 10 minutes to form a thin layer of RuO<sub>2</sub>. Thicker layers were obtained by repeating twelve times the process of applying the metal salt layer and subsequent thermal decomposition.

All electrochemical measurements were made by a potentiostat/galvanostat (Princeton Applied Research, Model 263). A three electrode cell system was used; TiO or Ebonex (or modified ones) electrode as a working electrode, a platinum wire spiral counter electrode, and a saturated calomel reference electrode (SCE). All potentials reported here are referred to SCE. Surface and intersection morphologies were examined with a scanning electron microscope (model S-2700, Hitachi).

Shown in Figure 1 are cyclic voltammograms (CVs) of the electrochemically deposited Ru thin layer and RuO<sub>2</sub> thin layer deposited by thermal decomposition of RuCl<sub>3</sub> on TiO or Ebonex (Ti<sub>4</sub>O<sub>7</sub>) electrodes in a 0.1 M HClO<sub>4</sub> electrolyte solution along with those of bare TiO and Ti<sub>4</sub>O<sub>7</sub> electrodes. Overpotentials of the oxygen evolution at bare Ebonex or TiO are very high, and oxygen evolution starts at about +2.0 V *vs.* SCE. Also, the conductive ceramics TiO and Ti<sub>4</sub>O<sub>7</sub> electrodes are very stable at high anodic potentials as can be seen in the figure. Oxygen evolution for electrochemically deposited Ru on Ebonex (Ru/Ti<sub>4</sub>O<sub>7</sub>) and for RuO<sub>2</sub> on Ebonex (RuO<sub>2</sub>/Ti<sub>4</sub>O<sub>7</sub>) starts at about 1.4 V, which is far less anodic

†This paper is dedicated Professor Woon-Sun Ahn in honor of his retirement.

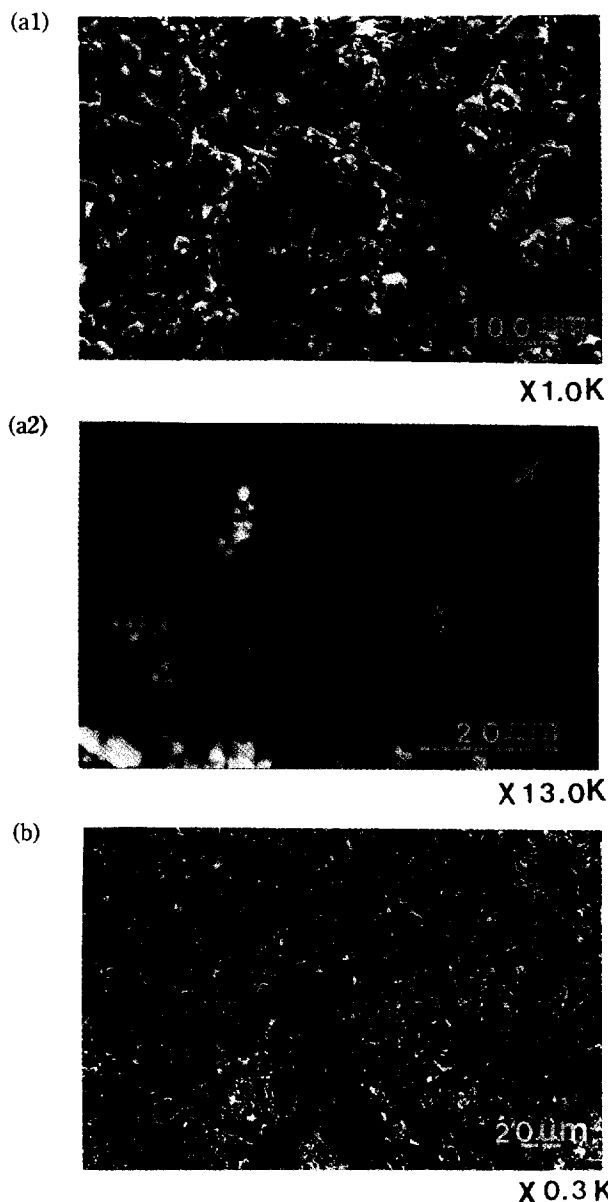


**Figure 1.** cyclic voltammograms recorded at 100 mV/sec in a 0.1 M HClO<sub>4</sub> electrolyte solution. (a1) bare Ebonex, (a2) Ru on Ebonex, (a3) RuO<sub>2</sub> on Ebonex. (b1) bare TiO, (b2) Ru on TiO, (b3) RuO<sub>2</sub> on TiO.

compared to 2.0 V at bare Ti<sub>4</sub>O<sub>7</sub> electrode and similar to the reported potential of oxygen evolution at RuO<sub>2</sub>.<sup>7</sup> Also, oxygen starts to evolve at about 1.2 V at Ru/TiO and RuO<sub>2</sub>/TiO. CV for Ru/TiO shows anodic and cathodic features in the far potential region, which corresponds to the oxidation of Ru to higher oxidation states and the cathodic process of the oxidized states of Ru during oxygen evolution process to the elemental Ru. On the other hand, RuO<sub>2</sub> coatings seem to be very stable at anodic potentials and during oxygen evolution. One of the primary advantages of the metal oxide coatings is known to be their acceptable electrochemical stability at anodic potentials. Capacitive charging currents for both RuO<sub>2</sub> on TiO and Ti<sub>4</sub>O<sub>7</sub> electrodes have been increased dramatically compared to those of the same apparent areas of bare electrodes.

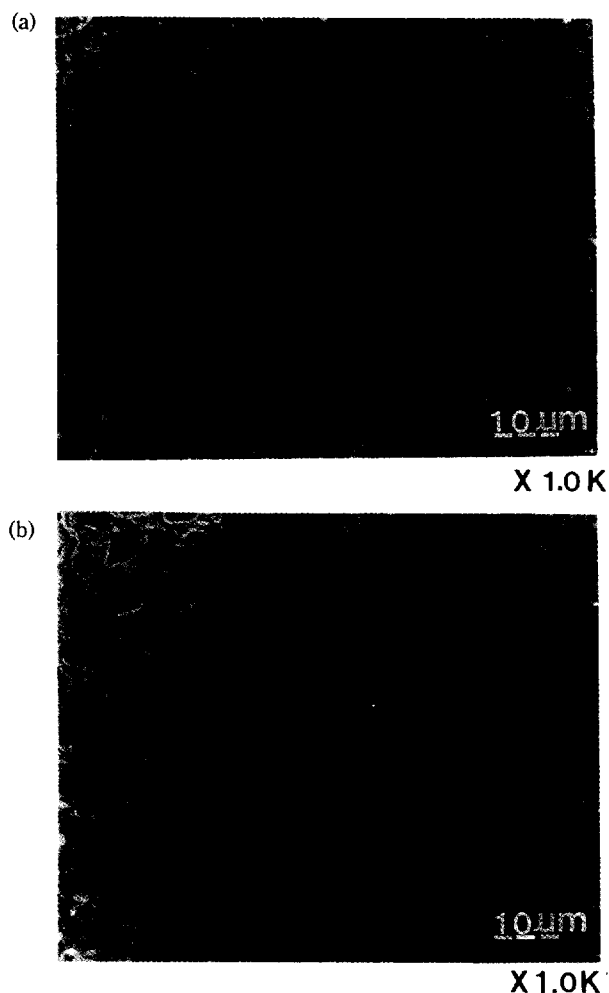
The morphologies of RuO<sub>2</sub> on TiO or Ti<sub>4</sub>O<sub>7</sub> were examined by SEM (Figure 2) RuO<sub>2</sub> coatings obtained by thermal decomposition show a large number of interconnected micro-cracks (mud cracks) that form discrete surface islands. Hence, the active surface area of the electrode has increased, which results in the large capacitive charging current for both RuO<sub>2</sub> on TiO and Ti<sub>4</sub>O<sub>7</sub> electrodes, as shown in Figure 1. Well known DSA type RuO<sub>2</sub> electrodes are usually prepared on a titanium substrate by thermal decomposition of ruthenium chloride. It is our observation that RuO<sub>2</sub> coatings can also be obtained well on conductive metal oxides such as TiO or Ti<sub>4</sub>O<sub>7</sub>.

The morphologies of Ru on TiO or Ti<sub>4</sub>O<sub>7</sub> are shown in



**Figure 2.** SEM photographs of RuO<sub>2</sub> deposited by thermal decomposition method on Ebonex or on TiO; (a) RuO<sub>2</sub> on Ebonex (Ti<sub>4</sub>O<sub>7</sub>), (b) RuO<sub>2</sub> on TiO.

Figure 3. The SEM photographs of the Ru surfaces on Ti<sub>4</sub>O<sub>7</sub> substrate show well grown grains compared to Ru surfaces on TiO substrate. Electrodeposition of ruthenium by applying a large overpotential at Ti<sub>4</sub>O<sub>7</sub> surface may result in the growth of the electrodeposited Ru grains. In both cases, the thickness of the Ru layer was less than one micrometer. Platinum thin films have also been electrochemically deposited on TiO and their electrochemical behavior is the same as Pt electrodes. On the other hand, Pt was not able to be deposited well electrochemically on Ti<sub>4</sub>O<sub>7</sub>. Even though the thickness of the Pt thin layer was about one micrometer, Pt thin layer on Ti<sub>4</sub>O<sub>7</sub> could not show the same electrochemical behavior as the bulk Pt electrode.<sup>15</sup> Hence, TiO was a better substrate than Ti<sub>4</sub>O<sub>7</sub> for platinum. In case of ruthenium, both TiO and Ti<sub>4</sub>O<sub>7</sub> are reasonably good electrode substrates. A more sys-



**Figure 3.** SEM photographs of electrodeposited Ru surfaces on (a) TiO and (b) Ebonex (Ti<sub>4</sub>O<sub>7</sub>).

tematic study on electrochemical behavior of noble metals and their oxides thin films on the conductive ceramics TiO and Ti<sub>4</sub>O<sub>7</sub> is currently under investigation on their characteristics as electrode substrates.

In conclusion, conductive ceramics, TiO and Ti<sub>4</sub>O<sub>7</sub> are chemically and mechanically stable and the overpotentials for oxygen evolution on the TiO and Ti<sub>4</sub>O<sub>7</sub> electrodes are very large. Both Ru and RuO<sub>2</sub>, well known electrochemical catalysts for oxygen evolution, can be deposited electrochemically and thermally, respectively, well onto TiO or Ti<sub>4</sub>O<sub>7</sub>. Thin layers of Ru and RuO<sub>2</sub> on either TiO or Ti<sub>4</sub>O<sub>7</sub> show electrochemical properties of Ru and RuO<sub>2</sub>, and the overpotentials for O<sub>2</sub> evolution have decreased dramatically.

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### Precursor Approach to Synthesis of New Ca-deficient Bi-2212 Superconductor

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Since the discovery of superconductivity in the Bi-based cuprate oxides,<sup>1,2</sup> numerous efforts have been made to synthesize single-phasic materials. Isolation of the materials from nominal compositions was often hampered owing to the multiphasic nature of the homologous series Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4</sub> (*n* = 1, 2, 3; hereafter denoted as Bi-22(*n* - 1)*n*). The Bi-2212 compound was generally obtained from a Ca-rich composition Bi<sub>2</sub>Sr<sub>1.5</sub>Ca<sub>1.5</sub>Cu<sub>2</sub>O<sub>8</sub> since the synthesis of the compound from the stoichiometric composition easily yielded ternary oxides rather than the final Bi-2212 product.<sup>3,4</sup> An excess amount of Ca in the starting composition is known to facilitate the formation of the Bi-2212 phase. The isolation of the Bi-2223 phase is even more complicated. The only successful way to synthesize the Bi-2223 phase is to add