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Journal of Alloys and Compounds 239 (1996) 111–113

Journal of ALLOYS AND COMPOUNDS

Effects of rare earth chlorides on the preparation of porous ruthenium oxide electrodes

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Received 2 September 1995; in final form 9 December 1995

Abstract

RuO_2–Re_2O_3/Ti (Ru:Re 7:3) electrodes prepared from the thermal decomposition of $RuCl_3$ and $ReCl_3$ were much more porous than conventional RuO_2/Ti electrodes. Porosities of the RuO_2–Re_2O_3/Ti electrodes depended on the ionic radii of the rare earth ions. Rare earth ions added to electrodes to prepare the RuO_2–Re_2O_3/Ti electrodes were completely dissolved in the acid solution. After dissolution of the rare earth ions, the voltammetric charges of the resulting RuO_2/Ti electrodes were still large. Rare earth chlorides were effective as pore initiators in preparing porous RuO_2/Ti electrodes, and were recovered after the preparation as catalysts.

Keywords: Ruthenium oxide; Rare earth chloride; Porous material; Pore initiator

1. Introduction

Ruthenium oxide electrodes such as RuO_2/Ti electrodes have been developed for the industrial uses of chlorine generating anodes in the chlorine–alkali process and oxygen generating anodes in electrolytic plating [1]. Ruthenium oxide electrodes have characteristically larger capacitances than metal electrodes. The application of large capacitances of ruthenium oxide electrodes to a supercapacitor system has been proposed [2,3]. The magnitude of capacitances depends on both the surface area and the specific voltammetric charge of a unit surface area of ruthenium oxides. Conventional RuO_2/Ti electrodes were made up of rather large RuO_2 particles (ca. 10–100 nm) and thereby insufficiently large surface areas. Capacitances are enhanced by dispersing ruthenium oxides with matrix oxides such as TiO_2, SnO_2 and Ta_2O_5. Although the matrix oxides are effective in reducing oxide particle sizes and enlarging surface areas, the specific voltammetric charge of a unit surface area also changes because of differences in electrode composition. Porous electrodes containing single ruthenium oxides are required for the characterization and design of ruthenium oxide electrodes. A novel method should be required for preparing porous RuO_2/Ti electrodes.

Recently, novel mesoporous carbons have been prepared by activating the carbon pitch with a rare earth ion [4]. Rare earth ions would be effective for preparing porous materials. We have found porous structures of RuO_2–La_2O_3/Ti electrodes prepared from the thermal decomposition of $RuCl_3$ and $LaCl_3$ (Ru:La 7:3) [5]. Lanthanum ions of the RuO_2–La_2O_3/Ti electrodes are completely dissolved in H_2SO_4; the porous structure remains unchanged during dissolution. Thus, porous RuO_2/Ti electrodes can be prepared from the RuO_2–La_2O_3/Ti electrodes. Voltammetric charges of the porous RuO_2/Ti electrodes were about 20 times larger than those of conventional RuO_2/Ti electrodes prepared by the thermal decomposition method. Lanthanum chloride plays an important role in preparing porous RuO_2/Ti electrodes.

In this study, a variety of rare earth chlorides was used to prepare porous RuO_2/Ti electrodes. The dependences of voltammetric charges and morphology on the ionic radii of rare earth ions were studied.

2. Experimental

The substrates of electrodes used in this study were commercial 99.5% titanium plates, 10×10 mm^2 in

0925-8388/96/$15.00
PII S0925-8388(96)02225-6

size, and rods, 1.6 mm in diameter. They were first etched in 10% oxalic acid solution at 80°C for 1 h, then washed with distilled water and dried. The electrodes were dipped into a mixture of n-butanol solution of 0.5 mol dm^{-3} $RuCl_3\ nH_2O$ (Ru 45.3%) and ethanol solution of 0.5 mol dm^{-3} $\mathrm{RECl_3}\ nH_2O$. After drying the substrates at 60°C for 10 min, they were calcined at 450°C in a preheated furnace for 10 min to decompose the metal salts into their respective oxides. For each specimen, this treatment was repeated 10 times.

The electrochemical cell consisted of a beaker equipped with a working electrode, a platinum plate counter electrode, and a silver–chloride reference electrode. The geometric surface area of the working electrode was 0.52 cm^2. A cyclic voltammogram was recorded by sweeping the electrode potential at 50 mV s^{-1} in a 0.5 mol dm^{-3} H_2SO_4 aqueous solution. Electrode potentials were referred to the reversible hydrogen electrode (RHE) scale. A Luggin capillary faced the working electrode at a distance of 2 mm. Voltammetric charges (q^*) corresponding to active surface areas were determined by integrating the enclosed area of the cyclic curves between 0.30 and 1.10 V (Fig. 1). The surface morphology of the electrodes was observed using a high resolution scanning electron microscope (Jeol JSM-6000F).

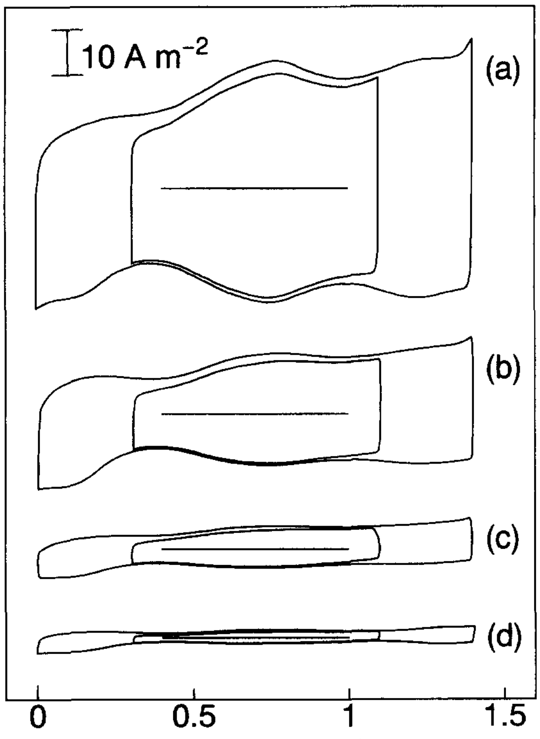

Fig. 1. Cyclic voltammograms for novel RuO_2/Ti electrodes prepared from (a) RuO_2–La_2O_3/Ti (Ru:La 7:3), (b) RuO_2–Eu_2O_3/Ti (Ru:Eu 7:3) and (c) RuO_2–Yb_2O_3/Ti (Ru:Yb 7:3) electrodes compared with (d) that for a conventional RuO_2/Ti electrode in 0.5 mol dm^{-3} H_2SO_4 swept at 50 mV s^{-1}.

3. Results and discussion

Cyclic voltammograms at the steady state in H_2SO_4 for RuO_2–La_2O_3/Ti (Ru:La 7:3), RuO_2–Eu_2O_3/Ti (Ru:Eu 7:3) and RuO_2–Yb_2O_3/Ti (Ru:Yb 7:3) electrodes are compared with those for conventional RuO_2/Ti electrodes prepared by the thermal decomposition method. Voltammetric charges q^* for RuO_2–La_2O_3/Ti (Ru:La 7:3) electrodes were one order of magnitude higher than those for conventional electrodes. Even RuO_2–Yb_2O_3/Ti (Ru:Yb 7:3) electrodes have still larger surface areas than those for conventional electrodes. The order for voltammetric charges of RuO_2–RE_2O_3/Ti (Ru:RE 7:3) electrodes is essentially the same as that obtained for radii of rare earth ions in electrodes. Fig. 2 shows the dependence of voltammetric charges of RuO_2–RE_2O_3/Ti (Ru:RE 7:3) electrodes on the radii of rare earth ions. The voltammetric charge increased with increasing rare earth ion radius.

It was noted that no RuO_2–RE_2O_3/Ti (Ru:RE 7:3) electrode contained any rare earth ion after reaching the steady state of cyclic voltammograms. Rare earth ions were completely dissolved in H_2SO_4 to form novel RuO_2/Ti electrodes at the steady state of cyclic voltammograms. The voltammetric charge depended on both the surface area and the specific charge on a unit surface area. Specific charges on a unit surface area of both novel and conventional RuO_2/Ti electrodes would be equivalent because the novel electrodes after dissolution of rare earth ions have the same composition as conventional electrodes. Therefore, novel electrodes have a much larger surface area

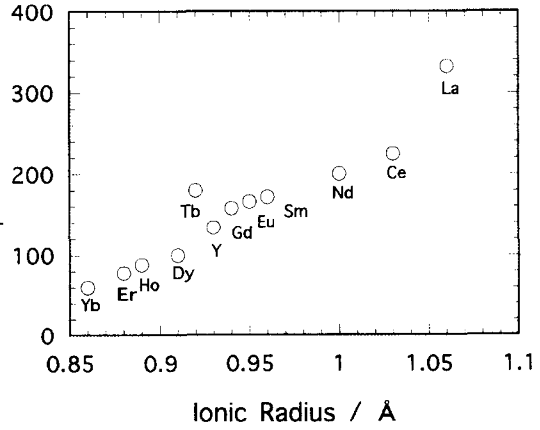

Fig. 2. Dependence of rare earth ion radii in precursor RuO_2–RE_2O_3/Ti (Ru:RE 7:3) electrodes on voltammetric charges of resulting porous RuO_2/Ti electrodes in 0.5 mol dm^{-3} H_2SO_4 swept at 50 mV s^{-1}.

than conventional electrodes. Rare earth ions are effective for preparing porous structures.

Voltammetric charges of RuO_2–Re_2O_3/Ti (Ru:Re 7:3) electrodes were also large before the dissolution of rare earth ions. Porous structures are formed not by the dissolution of rare earth ions, but during the thermal decomposition with rare earth chloride. Fig. 3 shows microstructures of RuO_2–La_2O_3/Ti (Ru:La 7:3), RuO_2–Eu_2O_3/Ti (Ru:Eu 7:3) and RuO_2–Yb_2O_3/Ti (Ru:Yb 7:3) electrodes before the dissolution of rare earth ions. The most porous structure was observed in RuO_2–La_2O_3/Ti (Ru:La 7:3) electrode, which exhibited the maximum voltammetric charge (Fig. 3(a)). The order of porosity was the same as that obtained for voltammetric charge. Large rare earth ions such as a lanthanum ions enlarged the surface area. The size of rare earth ions determined the pore size of the RuO_2/Ti electrodes. It is likely that rare earth chlorides act as pore initiators. The pore sizes evaluated from Fig. 3 were larger than the ion sizes. The pore formation is caused not by the dissolution of rare earth ions, but by disordering ruthenium oxide clusters during thermal decomposition with rare earth chloride. The coordination of rare earth ions to ruthenium oxide clusters is critical for the pore formation. The mechanism of pore initiation should be further studied.

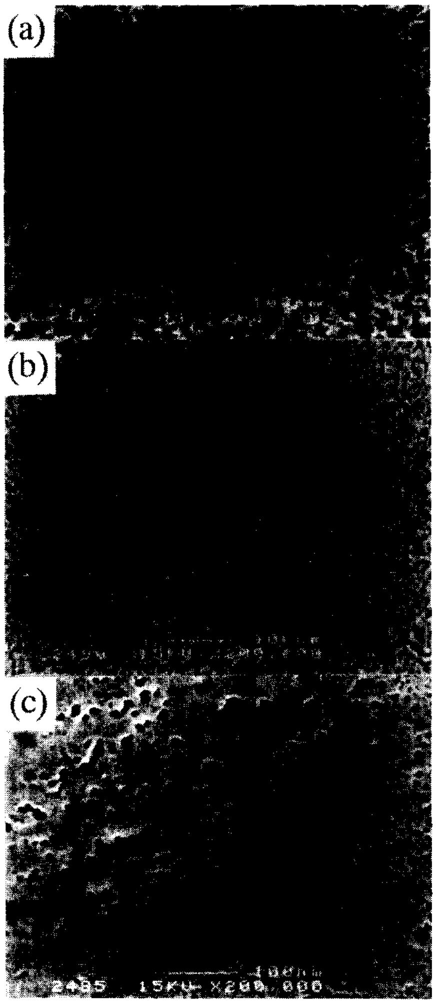

Fig. 3. High-resolution scanning electron micrographs of (a) RuO_2–La_2O_3/Ti (Ru:La 7:3), (b) RuO_2–Eu_2O_3/Ti (Ru:Eu 7:3) and (c) RuO_2–Yb_2O_3/Ti (Ru:Yb 7:3) electrodes.

The chemical properties of rare earth ions are similar to those of alkali earth ions. Voltammetric charges for RuO_2–CaO/Ti (Ru:Ca 7:3) electrodes are rather larger than RuO_2–La_2O_3/Ti (Ru:La 7:3). SEM images show, however, that RuO_2–CaO/Ti electrodes have a much less porous structure than RuO_2–La_2O_3/Ti (Ru:La 7:3). Calcium ions are not effective for pore formation, although they enlarge the specific charge on a unit surface area. Moreover, calcium ions in RuO_2–CaO/Ti (Ru:Ca 7:3) electrodes were not dissolved in any acid solution. Calcium ions are incorporated into the bulk structure of oxide electrode. However, rare earth ions in oxide electrodes can be recovered from acid solutions which dissolve rare earth ions. Rare earth ions will act as catalysts for preparing porous oxide materials.

Acknowledgements

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 06241107 from The Ministry of Education, Science and Culture.

References

[1] S. Trasatti, *Electrochim. Acta*, *36* (1991) 225.
[2] B.E. Conway, *J. Electrochem. Soc.*, *138* (1991) 1539.
[3] J.P. Zheng, P.J. Cygan and T.R. Jow, *J. Electrochem. Soc.*, *142* (1995) 2699.
[4] H. Tamai, T. Kakii, Y. Hirota, Y. Kumamoto and H. Yasuda, *Chem. Mater.*, in press.
[5] Y. Murakami, Y. Shimoda, T. Kondo, H. Kaji, K. Yahikozawa and Y. Takasu, in preparation.