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FOREIGN METAL-DOPED SnO_2 FILM ANODES FOR OXYGEN AND CHLORINE EVOLUTION

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The anodic characteristics of foreign metal-doped SnO_2 film electrodes, prepared by the thermal decomposition method, were studied in 1M KOH and 3M NaCl solutions. As a result, it was found that such electrodes have very attractive properties as anodes for oxygen and chlorine evolution.

Thin semiconducting SnO_2 films on glass or quartz have been used as indicator electrodes in various electroanalytical investigations.$^{1)}$ Such electrodes are well known to have low electric resistance, high mechanical resistance, good chemical resistance and relatively high hydrogen overvoltage.$^{1)}$ It might be expected that pyrolytic films of SnO_2 on metal substrates are utilized as anode materials for electrochemical processes. In connection with this, very recently Chertykovtseva et. al.$^{2)}$ briefly studied the electrochemical activity of a SnO_2 film electrode (Ti/SnO_2) at high anodic potentials in 0.5M H_2SO_4 and 1M HCl solutions. However, such pyrolytic films of SnO_2 are essentially a n-type semiconductor,$^{2)}$ and hence the oxygen and chlorine evolution reactions on the Ti/SnO_2 electrode could proceed at substantial rates only when the potential was made very highly anodic. On the other hand, the present authors$^{3)}$ have found in the course of studying on DSA-type battery grids that some Ti electrodes with oxide coatings mainly composed of SnO_2, such as $Ti/SnO_2-SbO_x-RuO_2/\beta-PbO_2$ and $Ti/SnO_2-SbO_x-IrO_2/\beta-PbO_2$, have a promising character as a positive grid in lead-acid batteries. In this work, foreign metal-doped SnO_2 film electrodes (Ti/SnO_2-MO_x) were prepared by the thermal decomposition method and their anodic characteristics were briefly examined in 1M KOH and 3M NaCl solutions. The intention of doping of the foreign metals in SnO_2 was to increase the electric conductivity and electrocatalytic activity.

The test electrodes were prepared in the following manner. Solutions of $SnCl_4$ and doping metal chlorides, such as $SbCl_3$, $RuCl_3 \cdot H_2O$, $PdCl_2$ and $H_2PtCl_6 \cdot 6H_2O$, in 20% HCl were mixed and a required amount of the resulting solution was applied to one side of a cleaned Ti disk (2.54cm^2) in 6 sequential coatings. After each coating, the solution was dried at a moderate temperature (below 100°C) in a drying oven and then placed in a preheated furnace at 450°C for 10 min. The sample was cooled between each of the first 5 coatings. After the final coating, it was heated at 450°C for 1 hr to complete the thermal decomposition and then cooled. The amounts of SnO_2 and MO_x loadings were $1x10^{-5}$ and $5x10^{-7}$mol of metal/cm^2, respectively. The existing form of the metals (preferably written in the form of metal oxides, MO_x, in this paper) doped in SnO_2 is still unknown though some XPS data for Pt-doped SnO_2 electrodes have been presented by Katayama.$^{4)}$ In addition to this type of electrodes (Ti/SnO_2-MO_x), some noble metal oxide-coated Ti electrodes (Ti/MO_x) with MO_x loadings of 1×10^{-5}mol of metal/cm^2 were also prepared by the same procedure. In the anodic polarization measurements, the test electrodes were preliminarily subjected to anodic polarization for 5 min at the highest current density to be studied (10mA/cm^2) and then the current density was lowered stepwise at intervals of 3 min. The potentials were measured with respect to a hydrogen electrode in the same solution (HE) or a saturated calomel electrode (SCE). The ohmic drop between the test electrode and the tip of the Luggin capillary was uncorrected in the curves shown below because it was negligibly small.

The anodic polarization curves obtained in 1M KOH solution are shown in Fig.1. The data obtained for the Ti/SnO_2-SbO_x electrode are excluded in the figure since the potentials were very highly anodic and unstable under the galvanostatic condition. It therefore seems most likely that the Ti/SnO_2-SbO_x electrode is undesirable for its practical use in water electrolysis unless it is irradiated. On the other hand, the noble metal-doped SnO_2 electrodes (Ti/SnO_2-MO_x) behaved like a metallic electrode and exhibited a variety of oxygen overvoltages, depending on a kind of doping metals. The oxygen overvoltage increased in the order of the Ti/SnO_2-RuO_2, Ti/SnO_2-PdO_x and Ti/SnO_2-PtO_x electrodes. This order is the same as that obtained for the Ti/MO_x electrodes. In any case, one or two linear Tafel lines were observed, whose slopes approximately corresponded to those observed on the Ti/MO_x electrode. Thus, the doping effect reflects the electrocatalytic activity for the oxygen evolution reaction of the doping metal. These findings are of interest in connection with the control of oxygen overvoltage of the anodes in various electrolytic fields.

The anodic polarization curves obtained in 3M NaCl solution are shown in Fig.2, in which the data obtained for the Ti/SnO_2-SbO_x electrode are excluded for the same reason as that described before. Evidently, all polarization curves of three Ti/SnO_2-MO_x electrodes are almost the same and very close to the Ti/RuO_2 and Ti/PdO_x electrodes. This means that the doping of noble metals exceedingly improves the electrocatalytic activity as well as electric conductivity of the SnO_2 film on the Ti base. These results are particularly interesting from theoretical and practical points of view. Hence, one can expect to develop a new SnO_2 anode having virtually the same electrocatalytic activity for chlorine evolution but much less quantity of noble metals than the commercial DSA. Somewhat similar studies to this have recently been made by the present authors5) for MnO_2-MO_x systems and by a Russian group6) for a Ti/Co_3O_4-RuO_2 system.

The disparity of doping effects between oxygen and chlorine evolution may be attributable to the difference in electrocatalytic activity of SnO_2 itself between these two reactions. The detailed works on the electrocatalytic mechanism and stability of the Ti/SnO_2-MO_x electrodes are now in progress.

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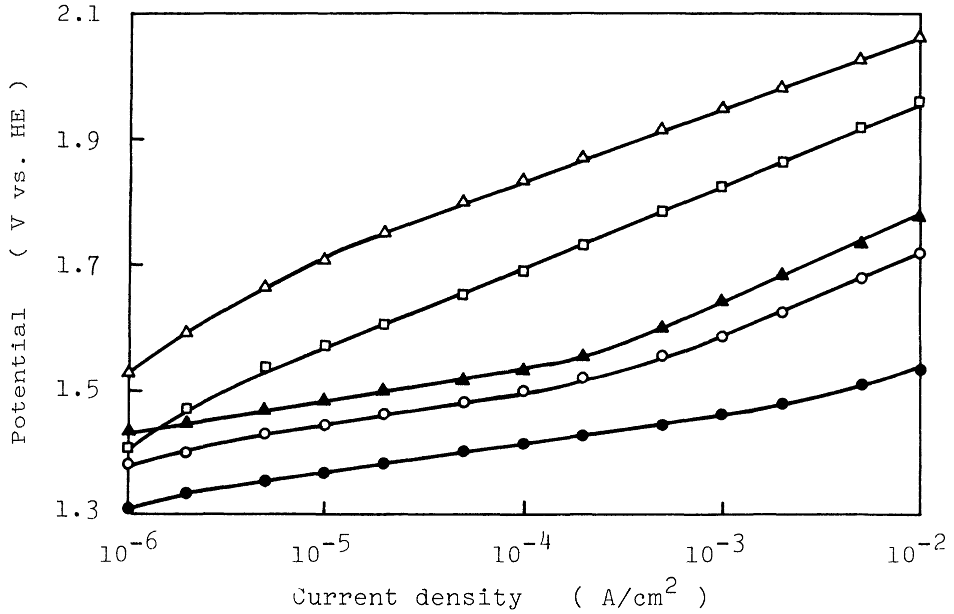

Fig.1 Anodic polarization curves in 1M KOH solution at 30°C. Oxygen passed through the solution.

○ : Ti/SnO_2-RuO_2, □ : Ti/SnO_2-PdO_x,
△ : Ti/SnO_2-PtO_x, ● : Ti/RuO_2,
▲ : Ti/PtO_x.

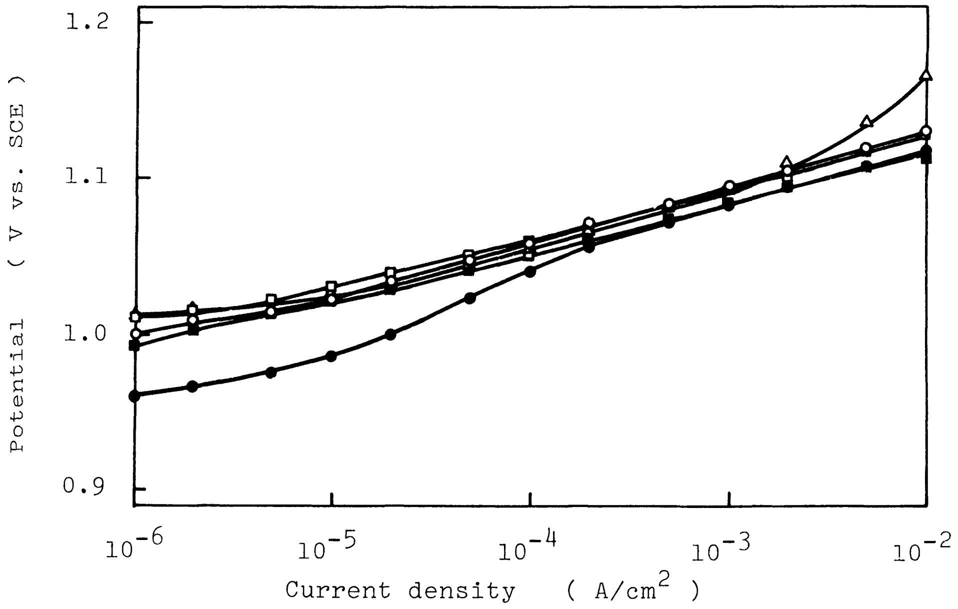

Fig.2 Anodic polarization curves in 3M NaCl solution at 30°C. Nitrogen passed through the solution.

○ : Ti/SnO_2-RuO_2, □ : Ti/SnO_2-PdO_x,
△ : Ti/SnO_2-PtO_x, ● : Ti/RuO_2,
■ : Ti/PdO_x

References

1) Z. Galus, " Encyclopedia of Electrochemistry of the Elements," Vol.IV, Ed. by A. J. Bard, Marcel Dekker, Inc., New York, N.Y.(1975), p.223.
2) T. A. Chertykovtseva, D. M. Shub, and V. I. Veselovskii, Élektrokhimiya, 14, 275(1978).
3) M. Inai, C. Iwakura, and H. Tamura, Extended abstract (C-6) presented at the 19th Battery Symposium of the Electrochemical Society of Japan, Tokyo, November, 1978.
4) A. Katayama, Extended abstract (B116) presented at the '78 Fall Meeting of the Electrochemical Society of Japan, Tokyo, October, 1978; Chem. Lett., 1978, 1263.
5) M. Morita, C. Iwakura, and H. Tamura, Electrochim. Acta, in contribution.
6) V. V. Losev, Private communication; Ya. M. Kolotyrkin, Extended abstract (No.19) presented at the 3rd Japan-USSR Seminar on Electrochemistry, Kyoto, November-December, 1978.

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