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# ANODIC CHARACTERISTICS OF Fe-SUPPORTED $Co_3O_4$ ELECTRODES IN ALKALINE SOLUTION

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Fe-supported $Co_3O_4$ electrodes were prepared by the thermal decomposition method and their anodic characteristics were studied in 1M KOH solution. As a result, it was found that the electrodes prepared at relatively low temperatures have very attractive properties as an anode for oxygen evolution.

Electrocatalysts for the oxygen evolution reaction are of special importance in water electrolyzers since the oxygen overvoltage is usually the main cause of efficiency losses in such devices. According to the published works,1) the $RuO_2$ electrode prepared by a thermal decomposition method does appear attractive as an anode for oxygen evolution though a problem to be solved is the reduction in material cost. Up to the present time, there seems to have been only a few publications on the oxygen evolution reaction at DSA-type oxide electrodes with a base metal.2) The electrochemical properties of spinel-type $Co_3O_4$ and related oxides such as $NiCo_2O_4$ and $Fe_xCo_{3-x}O_4$ ($0 \leq x \leq 3$) have been reported in connection with the chlorine evolution and oxygen reduction reactions.3) However, the electrochemical data for the anodic evolution of oxygen on such electrodes are limited.4) In the present work, Fe-supported $Co_3O_4$ electrodes ($Fe/Co_3O_4$) were prepared by the thermal decomposition method and their anodic polarization characteristics were studied in 1M KOH solution. The intention of employing a Fe substrate was to increase the electric conductivity and electrocatalytic activity by the formation of mixed crystals or solid solutions at the $Fe/Co_3O_4$ interface during the thermal decomposition.

The test electrodes ($Fe/Co_3O_4$) were prepared by the following procedure: An aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ was applied to one side of a cleaned Fe disk (2.54$cm^2$) in 5 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 250, 350 or 450°C for 10 min. The sample was cooled between each of the first 4 coatings. After the final coating, it was heated at the same temperature as that described above for 1 hr to complete the thermal decomposition and then cooled. Hereinafter, the resulting electrodes will be referred to as $Fe/Co_3O_4$ (250°C), $Fe/Co_3O_4$ (350°C) and $Fe/Co_3O_4$ (450°C), respectively. The amount of $Co_3O_4$ loading was $1 \times 10^{-5}$ mol of Co/$cm^2$ in every electrode. The composition and surface morphology of these electrodes were examined by X-ray diffraction method and by scanning electron microscopy (SEM), respectively. The anodic polarization characteristics were measured in $O_2$-saturated 1M KOH solution at 30°C. In these measurements, the test electrodes were preliminarily subjected to anodic polarization for 2 hr 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 mercury (Ⅱ) oxide electrode (Hg/HgO/1M KOH, +0.926V vs. HE at 30°C).

The X-ray diffraction patterns for three different electrodes are shown in Fig.1. Several peaks assigned to $Co_3O_4$ and α-Fe were observed in the case of Fe/$Co_3O_4$ (250°C) and Fe/$Co_3O_4$ (350°C) whereas some additional peaks which could be assigned to CoO and $Fe_3O_4$ or $CoFe_2O_4$ were observed in the case of Fe/$Co_3O_4$ (450°C). $Co_3O_4$ is known to be stable against thermal decomposition to CoO up to 900°C.[3] In fact, any peaks of CoO were not observed for the samples in which Ti was used as a substrate metal instead of Fe. These observations suggest that a part of oxygen is removed from $Co_3O_4$ during its formation since Fe is easily oxidized by oxygen at 450°C. The $Co_3O_4$ layer formed at 250°C or 350°C is presumed to include a small amount of Fe though it could not be confirmed by this experiment. Furthermore, it is considered that $Co_3O_4$ in Fe/$Co_3O_4$ (250°C) is in high crystallinity, compared with that in Fe/$Co_3O_4$ (350°C). According to the SEM micrographs of the electrode surfaces, the surface modifications of Fe/$Co_3O_4$ (250°C) and Fe/$Co_3O_4$ (350°C) were almost the same and the surfaces seemed to be very rough. On the other hand, the oxide of the Fe/$Co_3O_4$ (450°C) surface was in granular form and was partly aggregated.

The anodic polarization curves of Fe and Fe/$Co_3O_4$ electrodes are shown in Fig.2. Evidently, the oxygen overvoltage of the Fe/$Co_3O_4$ electrodes is much lower than that of the Fe electrode. In any case, a linear Tafel line with the slope of about 50mV was observed. The relatively high oxygen overvoltage of the Fe/$Co_3O_4$ (450°C) compared with the Fe/$Co_3O_4$ (250°C) and Fe/$Co_3O_4$ (350°C) can be ascribed in part to the low roughness of electrode surface. In the case of the Fe/$Co_3O_4$ (450°C) electrode, the rise of potential at high current densities is probably due to the presence of resistive CoO in the oxide layer. The data obtained for the Ti/$Co_3O_4$ (350°C) electrode are also shown in Fig.2 for comparison. The oxygen overvoltage of the Fe/$Co_3O_4$ (350°C) electrode (0.35V at 10mA/$cm^2$) is much lower than that of the Ti/$Co_3O_4$ (350°C) electrode (0.50-0.52V at 10mA/$cm^2$). Such effect of substrate on the electrode performance may be ascribed to the formation of mixed crystals or solid solutions at the substrate/oxide interface during the preparation of the electrodes. Thus, the Fe/$Co_3O_4$ electrodes seem to be very attractive, because they have fairly high activity for oxygen evolution but entirely consist of inexpensive materials.

Furthermore, one might expect to improve the electrode characteristics, the electric conductivity and electrocatalytic activity, by employing more suitable substrates and by doping foreign metals in the $Co_3O_4$ layer.

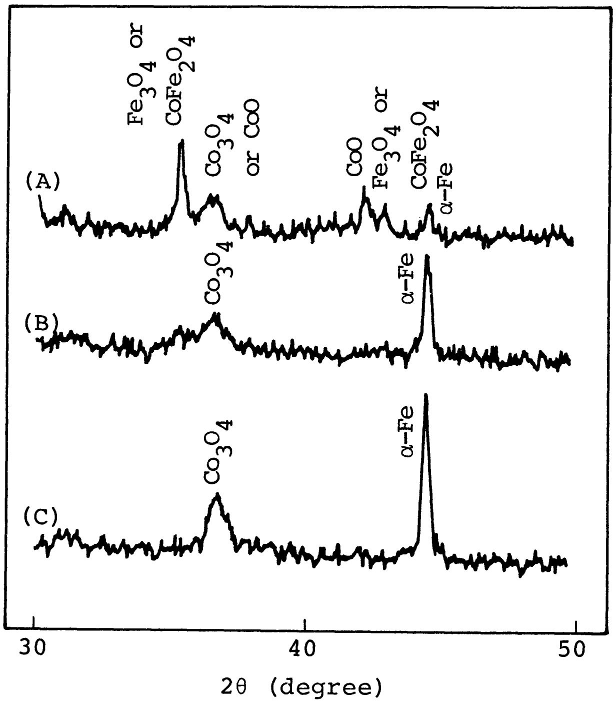

Fig.1 X-ray diffraction patterns of $Fe/Co_3O_4$ electrodes prepared at different temperatures. (A) 450°C, (B) 350°C, (C) 250°C.

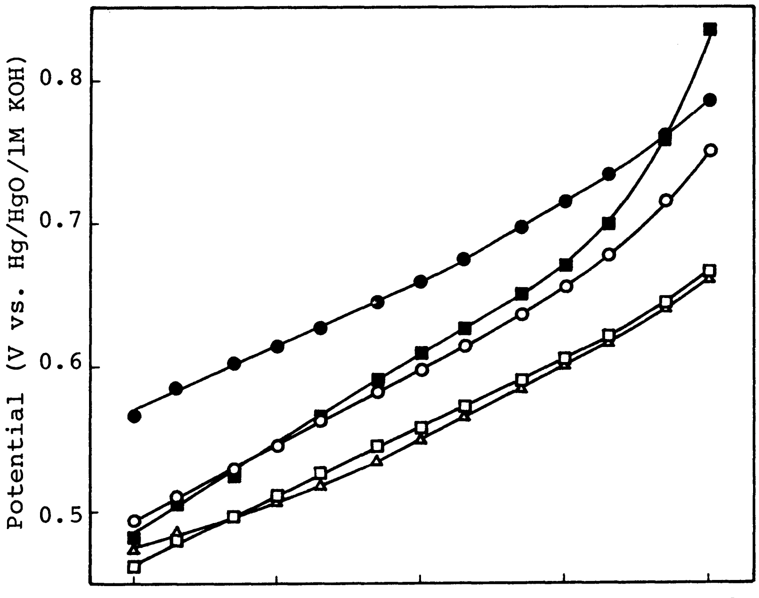

Fig.2 Anodic polarization curves obtained in $O_2$-saturated 1M KOH solution at 30°C. ○ :$Fe/Co_3O_4$ (450°C), □ :$Fe/Co_3O_4$ (350°C), △ :$Fe/Co_3O_4$ (250°C), ● :Fe, ■ :$Ti/Co_3O_4$ (350°C).

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