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SYNERGISM IN CHLORINE EVOLUTION ON NOBLE METAL-DOPED SnO_2 FILM ELECTRODES

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The dependence of the current density at given potentials on the RuO_2 loading in Ti/SnO_2-RuO_2 electrodes was investigated in 3 M $NaClO_4$ and 3 M NaCl solutions. The data show the existence of the synergism of SnO_2 and RuO_2 for chlorine evolution, but not for oxygen evolution.

The electrocatalytic activity of foreign metal-doped SnO_2 film electrodes (Ti/SnO_2-MO_x) for oxygen and chlorine evolution has recently been studied by Chertykovtseva et al.$^{1,2)}$ and the present authors$^{3,4)}$ with the intention of developing a new anode material. Our previous data$^{4)}$ showed that, in contrast to the oxygen evolution reaction, the chlorine evolution reaction on noble metal-doped SnO_2 film electrodes was independent of the kind of doping noble metals. Accordingly, the active center for the former reaction was considered to be at the noble metal site, whereas the probable mechanism proposed for the latter reaction involved the spillover of ·Cl radical from noble metal to Sn sites$^{4)}$. The purpose of this note is to report some experimental data to substantiate the above views; i.e. the absence and presence of a synergistic effect in the anodic evolution of oxygen and chlorine, respectively, on noble metal-doped SnO_2 film electrodes.

The test electrodes used mainly in this work were the Ti/SnO_2-RuO_2 electrodes having different RuO_2 loadings while maintaining the total amount of SnO_2 and RuO_2 at 1×10^{-5} mol/cm^2. These were prepared by thermally decomposing 20 % HCl solutions of $SnCl_4$ and $RuCl_3$ on a cleaned Ti substrate at 450 °C in the same manner as described previously$^{4)}$. The steady-state currents were measured when the test electrodes were anodically polarized at given potentials in 3 M $NaClO_4$ and 3 M NaCl solutions at 30 °C. The pH of each solution was adjusted to 2.0 by adding 6 %

$HClO_4$ prior to use. The solution was agitated by bubbling N_2 gas during the polarization measurement.

In this note, the molar activity of the Ti/SnO_2-RuO_2 electrode is defined as the current density at a given potential divided by the RuO_2 loading; this definition is quite similar to that given by Abbaro et al.$^{5)}$ for the specific activity of a platinized WO_3 electrode. For a system in which the support (SnO_2) takes no part, the molar activity of the Ti/SnO_2-RuO_2 electrode should remain constant with the variation of RuO_2 loading if the physical properties, such as surface area and electrical resistance, of the test electrode are virtually invariant.

The current densities at 1.180 V vs. SCE and the molar activities of the Ti/SnO_2-RuO_2 electrodes are plotted against the RuO_2 loading on log-log scale in Figs. 1 and 2 for oxygen and chlorine evolution, respectively. Similar results were obtained with Ti/SnO_2-IrO_2 electrodes. Since the data for these electrodes having the noble metal oxide contents less than 10^{-7} mol/cm^2 (mole fractions of noble metal oxides $\leqslant$ 0.01) were rather unreliable owing to the uncertainty about the oxide compositions, they will be excluded from the discussion.

For the oxygen evolution, an approximately logarithmic linear relationship exists between the current density and RuO_2 loading and moreover the current density shows a first-order dependence on the RuO_2 loading. Consequently, the molar activity is independent of the RuO_2 loading, as predicted for an inert support. This means the absence of the synergism of SnO_2 and RuO_2 in the oxygen evolution reaction on such electrodes. These facts support the view that the active center for the oxygen evolution reaction is at the Ru site. For the chlorine evolution, on the other hand, the current density tends to saturate as the RuO_2 loading increases. At relatively low RuO_2 loadings, its dependence of the current density is of an order more than second. The molar activity shows a maximum at a RuO_2 loading of 6-8 x 10^{-7} mol/cm^2. The existence of the maximum indicates SnO_2 being an active support or the presence of a synergistic effect$^{5,6)}$, and hence it strongly supports the spillover mechanism for the chlorine evolution reaction. The prerequisite for the discussion based on the molar activity of the Ti/SnO_2-RuO_2 electrode, or the constancy of the physical properties such as the surface area and electrical resistance with the variation of the RuO_2 loading, seemed to be practically fulfilled at least in the RuO_2 loadings more than 10^{-7} mol/cm^2, as will be discussed in some detail in a separate paper.

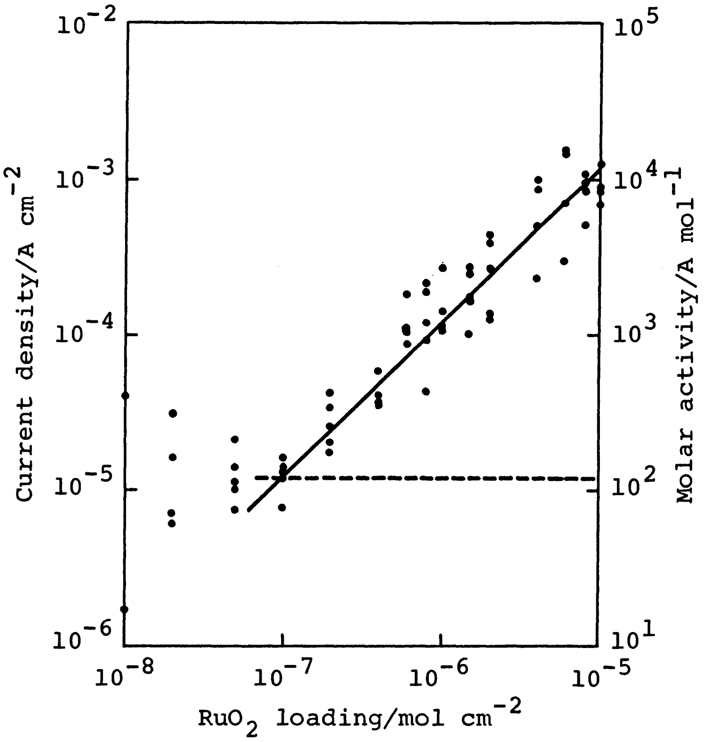

Fig.1 Plots of current density at 1.180 V vs. SCE (solid line) and molar activity of Ti/SnO_2-RuO_2 electrode (dashed line) against RuO_2 loading for oxygen evolution in 3 M $NaClO_4$ solution (pH 2.0) at 30 °C

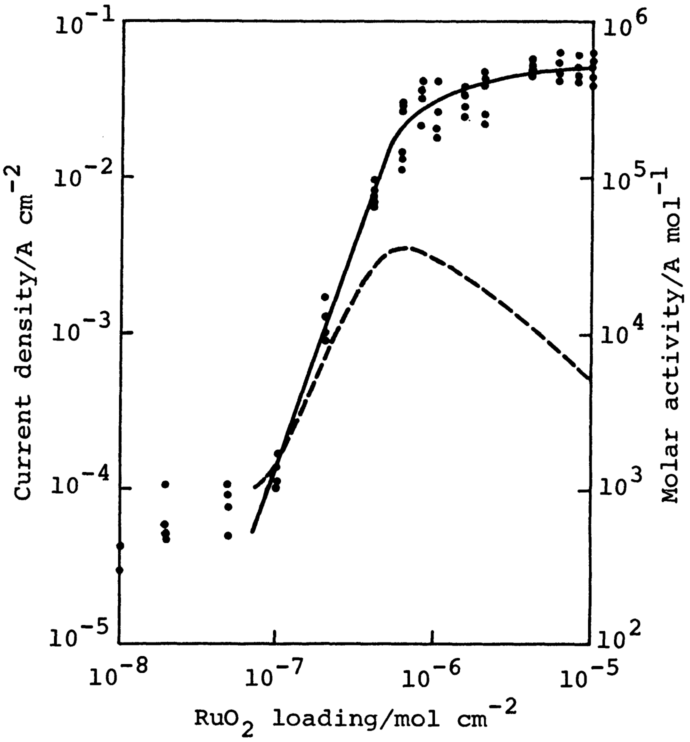

Fig.2 Plots of current density at 1.180 V vs. SCE (solid line) and molar activity of Ti/SnO_2-RuO_2 electrode (dashed line) against RuO_2 loading for chlorine evolution in 3 M NaCl solution (pH 2.0) at 30 °C

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