The Ternary Ru+Ir+Ce Porous Insoluble Catalytic Anodes for Oxygen Evolution in Acid Solution

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Insoluble catalytic anodes (ICA) have been applied extensively in electrochemical technology for their applications not only to the chlorine production in the chlorine-alkali process [1-2], but also to the oxygen evolution anodes in electrolytic plating [3]. These kinds of electrodes are characterized by a thin active coating (usually a few microns) deposited on a base metal, usually a valve metal (Ti, Zr, Ta, Nb). For the aspect of active coating, ruthenium oxide exhibits the lowest overpotential for oxygen evolution reaction [4]. However, it is not stable in acidic environments and also the oxygen overpotential increases with time. Therefore, ruthenium oxide have been mixed with stabilizing components which can be either conducting materials(IrO_2, Pt), or non-conducting thin oxides(TiO_2, ZrO_2, and Ta_2O_5) to improve the performance for oxygen evolution in acid solution [5].

In practical applications, a large surface area of the electrode is necessary for smaller overvoltage. Conventional RuO_2/Ti electrode was made up of rather large RuO_2 particles and thereby the real surface area is still not sufficiently large enough for good electrocatalysis. Cerium chloride is effective as pore initiators in preparing porous RuO_2/Ti electrode. For the binary structure of RuO_2-CeO_2/Ti electrode prepared from the thermal decomposition of $RuCl_3$ and $CeCl_3$, cerium ion is completely dissolved in acid solution and therefore the pores are induced [6].

In this study, Ti-supported electrodes of ternary composition $Ru_xIr_yCe_zO_2$/Pd/Ti (x+y+z=1) were prepared by thermal decomposition of chloride precursor mixtures. The electrochemical characteristics of various porous ternary-oxide electrodes for oxygen evolution from 1N H_2SO_4 solution were investigated by CV and AC impedance measurements. The experimental conditions are listed in Table 1. Experimental results shown in Table 2 indicate that increasing the CeO_2-content of the electrodes causes an increase in their active surface area, as supported by the values of the anodic voltammetric charge (q*) from CV and double layer capacitance (C_{dl}) from AC impedance. However, the charge transfer resistances (R_{ct}) of the electrodes were not all decreased as we expected.

As shown in Fig. 1, the behavior of $1/R_{ct}q^*$ as a function of composition suggests a synergistic effect is caused by CeO_2 addition. The synergistic effect is positive (improvement) at low CeO_2-contents (20~30 mol%) and negative (depressive) at higher CeO_2-contents (≧30 mol%). In addition to the remnants of cerium in the oxide layers, the reason of the negative synergistic effect is related to the blocking by oxygen bubbles in porous oxide textures, in which oxygen is more difficult to be stripped from active sites and transported through the porous textures outward to the surface. This would reduce the electrochemical active area, and therefore, high Ce content would result in the increase of R_{ct}. Based on $1/R_{ct}q^*$ behavior, best composition was found for electrodes with low CeO_2-content (20~30 mol%). Furthermore, $Ru_{0.6}Ir_{0.2}Ce_{0.2}O_2$ gave the best performance among these electrodes.

Reference

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Table 1 Experimental conditions.

Reference electrode	Ag/AgCl reference electrode
CV method :	
Voltage range	0-800 mV
Scan rate	50mV/s
AC impedance :	
Frequency range	60 kHz to 0.1 Hz
Amplitude	100mV
Measure C_{dl}	E=600mV
Measure R_{ct}	E=1200mV

Table 2 The values of anodic voltammetric charge (q*) from CV and double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}) from AC impedance for different composition electrode.

Electrode	q*(mC/cm^2)	C_{dl}(mF/cm^2)	R_{ct}(Ωcm^2)
$Ru_{0.6}Ir_{0.0}Ce_{0.4}O_2$	24.95	31.16	29.06
$Ru_{0.6}Ir_{0.2}Ce_{0.2}O_2$	18.48	21.23	0.41
$Ru_{0.6}Ir_{0.4}Ce_{0.0}O_2$	7.48	15.42	16.59
$Ru_{0.7}Ir_{0.0}Ce_{0.3}O_2$	19.96	27.51	4.51
$Ru_{0.7}Ir_{0.1}Ce_{0.2}O_2$	18.26	26.79	0.75
$Ru_{0.7}Ir_{0.2}Ce_{0.1}O_2$	10.24	18.18	10.14
$Ru_{0.7}Ir_{0.3}Ce_{0.0}O_2$	4.46	9.71	24.62

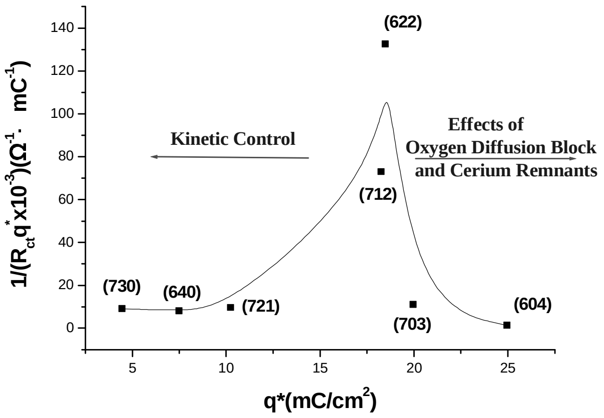

Fig. 1. Relation of q* with inverse of the product of R_{ct} and q*.