

Electrocatalytic Oxygen Reduction and Water-Oxidation on Transition Metal Ions-Doped MnO₂, RuO₂ and IrO₂ in Alkaline Aqueous Solutions

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1. Introduction

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are enormously important electrochemical reactions for energy conversion process (chemical energy to electrical energy and its reverse). The key technology in the energy conversion process is the fabrication of active electro-catalysts for both ORR and OER at the electrodes. Several studies have been reported with noble metals and metal oxides as bi-functional electro-catalysts for ORR and OER.¹⁻⁴ However, the efficient bi-functional electro-catalysts have not been developed due to anodic corrosion during the OER. Exhaustive examination has been done with transition metals-doped MnO₂, RuO₂, and IrO₂ to find the efficient bi-functional electro-catalysts.

2. Experimental

All catalysts were prepared by the precipitation of metal ions followed by annealing. For example, α -MnO₂ was synthesized by annealing at 350° C for 10 h after oxidative treatment of Mn(CH₃COO)₂ with KMnO₄. RuO₂-doped α -MnO₂ was prepared by annealing 350° C for 10 h at after adding RuCl₃ to the mixture of Mn(CH₃COO)₂ with KMnO₄. Electrochemical measurements were performed in 0.1 M KOH aqueous solution with the samples (α -MnO₂ or RuO₂-doped MnO₂) coated, rotating disk GC electrode. BET surface area of the as-synthesized particles were used to calculate the cathodic current density.

3. Results and Discussion

Figure 1 shows the *p*XRD profiles for α -MnO₂, RuO₂, and RuO₂-doped α -MnO₂ samples with simulated *p*XRD profiles of α -MnO₂ and RuO₂. The *p*XRD profiles of the synthesized α -MnO₂ (pnm, CaCl₂ type structure) and RuO₂ (P4₂/mnm, TiO₂ type structure) are consistent with their simulated profiles, indicating that the synthesized samples are free from the by-products. The reflection peak (110) of α -MnO₂ is shifted gradually to the lower diffraction angles with increasing the amounts of doping of RuO₂, indicating that incorporation of RuO₂ into MnO₂ lattice. .

ORR on these particle surfaces was examined with a rotating disk electrode in O₂-saturated 0.1 M KOH solution. Doping of RuO₂ into α -MnO₂ improved the

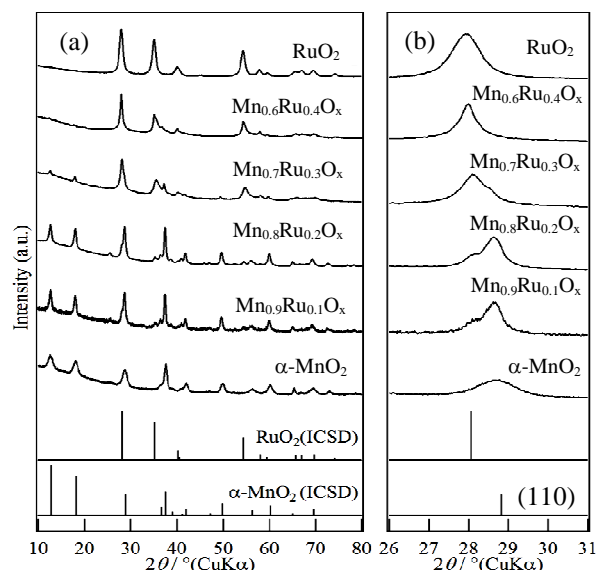


Fig. 1 *p*XRD patterns of synthesized Mn_{1-x}Ru_xO₂ particles (a) and the reflection peak for (110) plane (b).

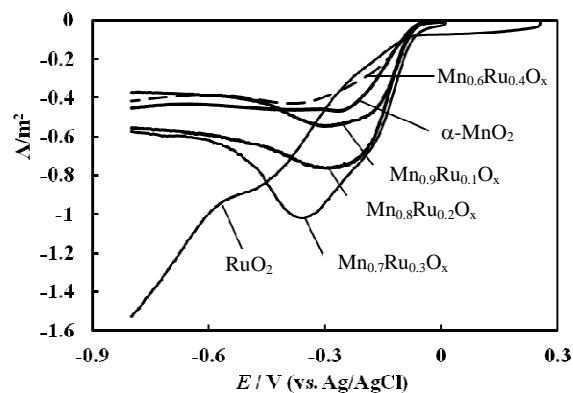


Fig. 2 Cyclic voltammograms of RuO₂-doped MnO₂ for oxygen reduction reaction in O₂-saturated 0.1 M KOH aqueous solution at 10 mV s⁻¹ and 2000 rpm.

ORR activity. The Mn_{0.7}Ru_{0.3}O₂ sample exhibited the highest current density, however, ORR activity decreased drastically when the doping of RuO₂ increased further than above 30%. It should be noted that pristine RuO₂ possesses both higher onset as well as reduction potential. The electrocatalytic activity of MnO₂, RuO₂, IrO₂ and transition metal **ion**-doped MnO₂, RuO₂ and IrO₂ towards ORR and OER would be discussed in the presentation.

4. References

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