

Doped MnO₂-based oxygen reduction and evolution catalysts for bifunctional cathodes in alkaline electrochemical power sources

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The development of a bifunctional catalyst for both oxygen reduction (ORR) and evolution (OER) reactions is of great interest for electrochemical power sources such as regenerative fuel cells and rechargeable metal/air batteries [1]. Manganese dioxide has been intensely investigated as a catalyst for ORR in alkaline batteries and fuel cells due to a unique combination of properties, i.e., low cost, abundance, environmental friendliness and promising electrocatalytic activity for ORR [2]. However, with respect to the bifunctional cathode, some issues such as low electrocatalytic activity for OER, poor recharging and complex charge-discharge behavior, limits the application of MnO₂ as a catalyst for both OER and ORR in rechargeable alkaline batteries [3].

Our research is aimed at the development of highly active MnO₂-based catalysts for both ORR and OER with long cycle life by doping MnO₂ with non-precious metal compounds. The mechanisms for OER and ORR of the mixed catalysts and the role of dopant species are investigated by a combination of surface characterization methods and electrochemical techniques.

In the present work, three different dopants, i.e., LaNiO₃, LaCoO₃ and Nd₃IrO₇, were synthesized via co-precipitation and thermal methods. Various catalyst inks were made by 1 hr. sonication of a mixture composed of MnO₂ (Sigma-Aldrich GmbH manganese (IV) dioxide), Vulcan XC-72R, dopants (LaNiO₃, LaCoO₃ or Nd₃IrO₇), isopropanol, water, 5 wt% Nafion solution and 60 wt% PTFE suspension. The weight ratios of the components were 1:1:1:50:16:0.6:0.6, respectively. Next, specified volumes of the catalyst inks were drop-casted on a 6 mm diameter carbon cloth (with 40 wt% PTFE from Fuel Cell Earth Inc.) to reach a MnO₂ and dopant loading of 0.5 mg cm⁻² each. Afterwards, the electrodes were dried in an oven at 70 °C for 1 hr.

Cyclic voltammetry tests were performed in O₂ saturated 6 M KOH at 293 K to investigate the electrocatalytic activity of the doped MnO₂-based catalysts for both OER and ORR. The longer-term durability of the electrodes was also investigated. Experiments using the freshly prepared electrodes showed active OER behavior for all the doped samples. Based on the Tafel slope (*b*) and exchange current density (*i*₀) values, the best performance in the OER kinetic region was observed for the MnO₂-LaNiO₃. In the ORR kinetic region, however, the MnO₂-Nd₃IrO₇ catalyst showed the highest activity.

The electrocatalytic durability was tested by performing 100 repeated OER-ORR voltammetric cycles. A gradual diminishing of the electrocatalytic activity toward OER and ORR was observed in all cases. After 100 cycles the performance dropped up to 60% of the initial stage activity for some samples.

Interestingly, a healing effect was observed in the performance of all catalysts when the electrodes were kept at rest under open circuit conditions in 6 M KOH solution after the durability tests for certain periods of time (between 6 to 34 days). Not only all the samples regained their initial (fresh) catalytic activity toward both OER and ORR but also considerable enhancements were found in their ORR

and OER electrocatalytic activities. Fig 1-a and 1-b show the OER and ORR voltammograms, respectively, after 6 and 34 days of rest time following durability testing. The OER overpotential for MnO₂-LaCoO₃ decreased with 162 mV after 6 days of immersion in the 6 M KOH solution following durability testing (Fig. 1-a). In the ORR region, MnO₂ doped with Nd₃IrO₇ still provided the lowest ORR overpotential (Fig. 1-b), which is far better than the ORR behavior reported in the literature for PdO-RuO₂, CoMn₂O₄ and even MnO₂-N doped carbon nanotubes [4].

Our results suggest that MnO₂-LaCoO₃ as well as MnO₂-Nd₃IrO₇ catalysts are promising candidates for cathode materials in rechargeable alkaline batteries and fuel cells. The presence of the dopant improved both the OER and ORR activities in comparison to the base MnO₂ electrode [5]. The healing effect during rest-time at open circuit in 6 M KOH merits further investigation due to significant improvements of both OER and ORR electrocatalytic activities following extensive cycling.

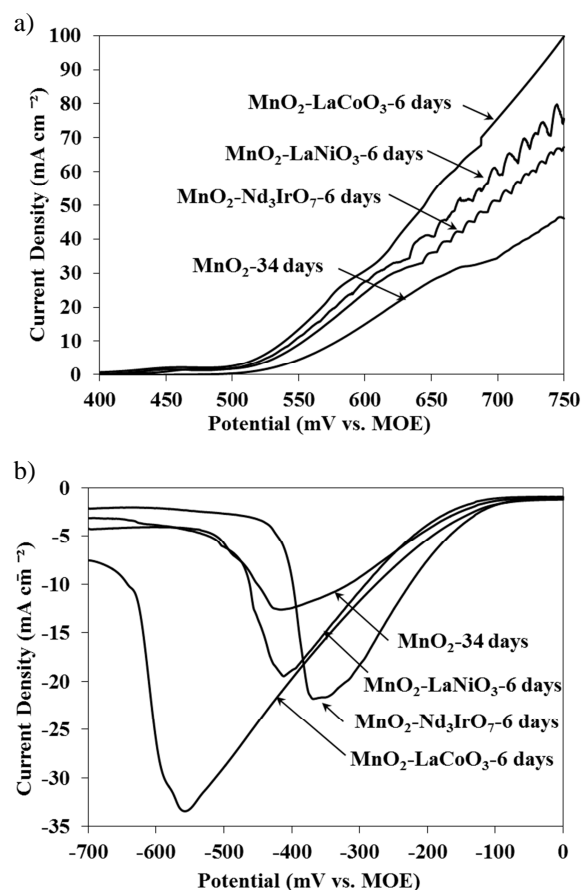


Fig 1. The healing effect of rest-time (6 and 34 days) at open-circuit in 6M KOH following durability testing (i.e., 100 cycles). Electrodes prepared on 40 wt% PTFE treated carbon cloth and tested in O₂ saturated 6 M KOH solution at 293 K. The MnO₂ and dopant loading 0.5 mg cm⁻² each. a) OER voltammograms, b) ORR voltammograms.

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