

Peroxide generation features: an in-situ diagnostic tool in electrocatalysis of oxygen reduction reaction (ORR)

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INTRODUCTION

Two e^- reduction of oxygen to hydrogen peroxide (H_2O_2) occurs parallel to the $4e^-$ reduction to water. The formation of peroxide is deleterious to the components of membrane electrode assembly (MEA) in a fuel cell, particularly the membrane electrolyte and catalyst. Moreover, it results in a lower cell voltage or efficiency due to lower free energy of formation of H_2O_2 when compared to the major product water. Thus, H_2O_2 formation is determined while investigating new catalyst formulations and it is often found to be less than 5% at practical fuel cell operating voltage of ~ 0.5 V. We report on the possibility of using peroxide characteristics as an in-situ diagnostic tool in exploring the catalyst surface during oxygen reduction reaction.

EXPERIMENTAL

Catalyst ink was prepared by sonicating a mixture of catalyst, isopropyl alcohol, Nafion and water. The catalyst ink was drop-casted onto a rotating ring disk electrode (RRDE). All electrochemical measurements were conducted using a three electrode system at room temperature. The oxygen reduction voltammogram was recorded with oxygen-saturated 0.1 M $HClO_4$ at 1600 rpm with a scan rate of 20 mV s^{-1} . Hydrogen peroxide formation, parallel to the oxygen reduction reaction to water, was determined using the RRDE technique. The ring potential was held at 1.2 V and the disk potential was scanned from 0.05 to 1.05 V. The peroxide formation was quantified using the well-established method reported in the literature [1].

RESULTS AND DISCUSSION

Fig. 1 shows the peroxide formation features as a function of potential parallel to the ORR reaction. The ring current is quite negligible at potential above ~ 0.7 V and it gradually rises at potential below 0.7 V in the reverse scan and further rises at potential below 0.3 V in the H_{upd} region. This behavior is usually observed on the state-of-the-art catalyst Pt. We investigated the peroxide features as a function of potential on a few promising catalysts under investigation. Though the features are similar to that of Pt, it can provide significant insight to the reaction mechanism and can map the catalyst surface as a function of potential. The peroxide generation features recorded in the forward and backward scans of the ORR is correlated to the respective voltammograms recorded in argon-saturated 0.1 M $HClO_4$ electrolyte. We observe that peroxide features sheds light on the role of OH and oxide species on ORR and on the role of transition metal in stabilizing the precious metal at higher potentials.

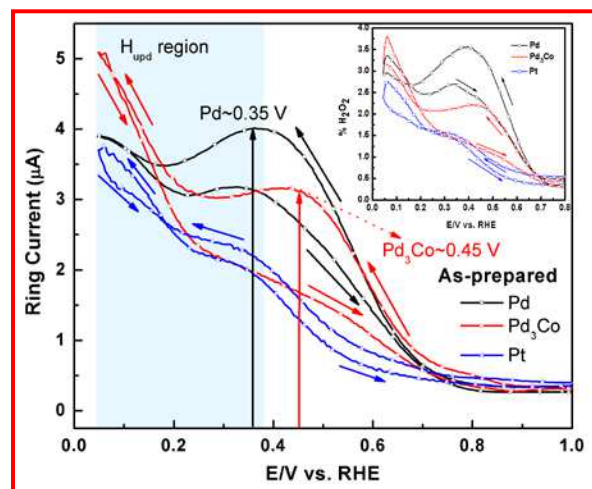


Fig. 1 Ring currents with as-prepared carbon-supported Pd, Pd_3Co , and Pt at a scan rate of 20 mV s^{-1} with 1600 rpm in oxygen-saturated 0.1 M $HClO_4$ at room temperature; inset to Fig. 1 shows the fraction of H_2O_2 formation as a function of potential.

REFERENCES

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