ORR Measurements Reproducibility Using a RRDE

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The thin film rotating disk electrode (RDE) methodology has long been used to study the slow oxygen reduction reaction (ORR). It has specifically been adopted as an indispensable technique for evaluating the performance of fuel cell cathode catalysts. The mass activity and specific activity in the kinetic region (0.85-0.9V vs. RHE) are normally preferred as comparative criteria for different catalysts instead of the exchange current. However, the reported ORR catalyst activities significantly vary between research groups even with commercially available Pt/C catalysts (1). Several reasons explain this situation and include different catalyst ink compositions and film preparation techniques, measurement errors, the variability in the use of electrolyte ohmic loss and background current corrections, etc. This situation hinders the development of new catalysts because progress cannot be clearly established. Garsany et al at the Naval Research Laboratory (2) have developed a rotational drying method to prepare uniformly thin catalyst films for RDEs. Results have shown that film quality has a large impact on the ORR polarization curve and catalyst activities. Highly reproducible ORR results were obtained with thin catalyst films prepared with the rotational drying method in comparison to the traditional and stationary coating method.

Additional information about the ORR mechanism is available by quantifying the H_2O_2 intermediate formation rate using a rotating ring/disk electrode (RRDE). The RRDE is also a useful tool to study ORR catalysts contamination mechanisms because the adsorption of the contaminants on the surface not only reduces the catalyst real surface area but also favors the two electrons reduction process (3). However, H_2O_2 intermediate formation rates significantly vary (4,5) because values are relatively small, normally only reaching a few microamperes or a few % of the ORR current. In this work, the NRL rotational drying method was used to prepare thin film Pt/C electrodes. The reproducibility of both ring and disk currents for the ORR was evaluated.

Cyclic voltammetry scans were completed before ORR tests. Eight different films were prepared and evaluated. The Pt electrochemical area was calculated using the H_{UPD} desorption area between 0.05-0.4V vs RHE. A value of $83.5\pm1.9 m^2 g_{Pt}^{-}1$ demonstrates the high level of reproducibility achieved for all films. Fig. 1 shows highly reproducible ORR polarization curves. The mass activity at 0.9 V vs RHE was calculated and shown in the inset of Fig. 1 with an average value of $0.38\pm0.03 A\ mg_{Pt}^{-1}$. Fig. 2 shows the ring current reproducibility with the H_2O_2 fraction $X_{H_2O_2}$ of the total ORR current calculated with the following equation:

$$X_{H_2O_2} = 2(I_R / N)/(I_D + (I_R / N)) \qquad [1]$$

where I_R represents the ring current, N is the collection efficiency and I_D is the disc current. The average H_2O_2 fraction is 0.76±0.17% at 0.3V vs RHE. The ring results are less reproducible in comparison to cyclic voltammetry and ORR polarization measurements. The reproducibility was deemed more than acceptable in view of the ring current low values and confirms that the rotational drying method leads to highly reproducible RDE and RRDE measurements.

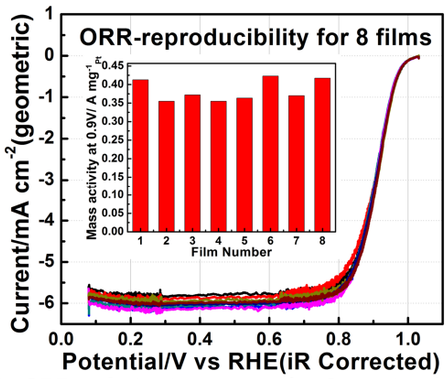

Fig. 1. ORR polarization curves for 8 rotational drying films in 0.1M $HClO_4$, 30°C, 20mV/s, 1600 rpm. The inset shows the corresponding mass activity.

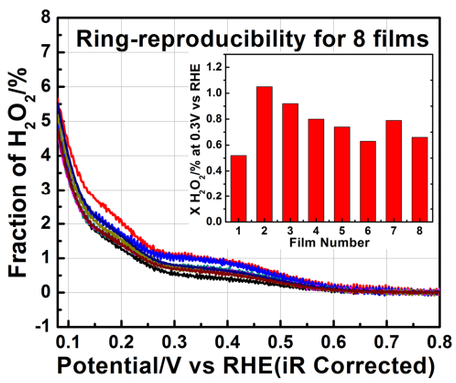

Fig. 2. Fraction of H_2O_2 formed during the ORR for 8 rotational drying films. Pt ring held at 1.2V vs RHE. The inset shows corresponding H_2O_2 fractions at 0.3V vs RHE.

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