

Electrochemical Quartz Crystal Microbalance Analysis of the Oxygen Reduction Reaction on BN Nanosheet Modified Gold

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Introduction:

Boron nitride nanosheets (BNNS) have been reported to be promising electrocatalysts for the oxygen reduction reaction (ORR) [1]. By depositing BNNS onto specific substrates (Au and Ni), the intrinsically insulating material can become excellent candidate for replacing expensive, rare, and sluggish Pt-based electrocatalysts currently used in most fuel cells. To further increase the catalytic activity of BNNS based electrocatalysts, it is necessary to understand the fundamental kinetics taking place on these materials. To this end, this study uses electrochemical quartz crystal microbalance (eQCM) to measure *in situ* adsorption and desorption oxygen.

Experimental Methods:

BNNS was synthesized through a liquid exfoliation method. Boron nitride (BN) powder was sonicated in IPA (3 mg/ml) for 96 hours. The resulting solution was centrifuged at 1500 rpm and the top of the supernatant was recovered for deposition. A 100 nm gold (Au) thin film deposited on an AT-cut quartz crystal (Hokuto Denko) was used as the working electrode for the eQCM electrodes. The electrodes were spin coated with 5 μ L of the resulting BNNS solution at 1000 rpm for 2 min. The electrodes were then dried under vacuum at 200°C for 2 hr.

The eQCM setup consisted of a platinum (Pt) wire counter electrode, a Ag/AgCl reference electrode, and a Teflon® eQCM electrode holder with the coated Au surfaces as the working electrode. A perchloric acid (0.1 M) electrolyte was used. Each electrode was cleaned for 1 hr by oxidation/reduction cycle (ORC) between -0.2 and +0.95 V (vs Ag/AgCl). QCM and EQCM measurements were first taken under deaerated conditions by bubbling Ar gas through the electrolyte for 1 hr. The electrolyte was then saturated with O₂ by bubbling O₂ gas through the electrolyte for 1 hr.

QCM and cyclic voltammetry (CV) measurements were simultaneously taken on an electrochemical measurement system (Hokuto Denko HZ-7000). Electrode surfaces were cleaned through ORC scanning between -0.2 and +1.5 V for 1 hr under both Ar-saturated and O₂-saturated conditions. QCM and CV data was then taken by scanning between -0.2 and +0.7 V. Each eQCM measurement was cycled ten times at each scan rate to ensure reproducibility and reversibility. The mass change (Δm) was estimated from the Sauerbrey equation [2]. The mass sensitivity was determined, through bulk Cu deposition, to be 4.58 and 4.78 ng/Hz cm² for the BNNS/Au electrode and the bare Au electrode, respectively. In this study, adsorbed materials were assumed to be thin and rigid and, thus, viscoelastic effects were neglected.

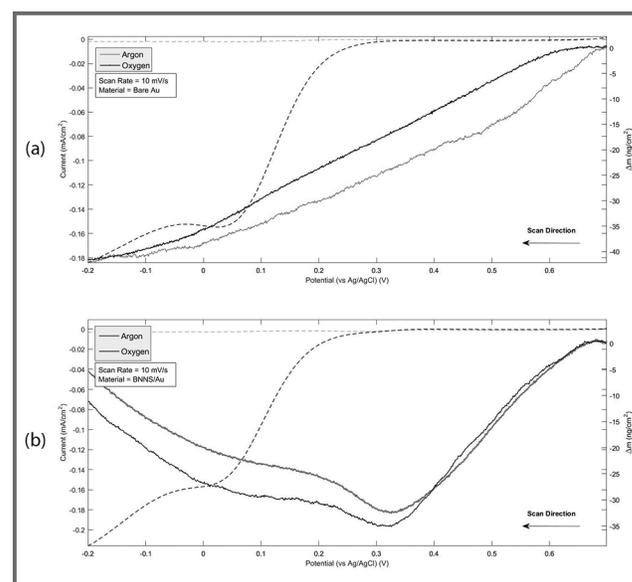


Figure 1: Reduction sweeps (left axis) and Δm (right axis) for bare Au electrode (a) and BNNS/Au (b).

Results and Discussion:

Figure 1 (a) and (b) show the CV and calculated Δm for both the bare Au and BNNS/Au samples, respectively. Both materials exhibit the large ORR reduction wave in the O_2 -saturated environment, whilst exhibiting negligible net-current in the Ar -saturated environment. The Δm data indicates that for both gaseous environments only net-mass desorption occurs on bare Au, while the BNNS/Au electrode experiences net-mass desorption until a potential of approximately +0.3V and then net-mass adsorption for the rest of the scanned potential range. This may indicate early onset hydrogen adsorption for BNNS/Au in the potential region less than +0.3, but more analysis is needed to isolate the identity of this adsorbing species.

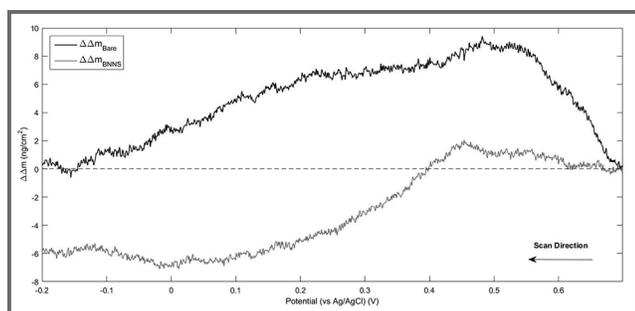


Figure 2: Mass of adsorbed oxygen with respect to potential for bare Au and BNNS/Au.

The mass difference between O_2 -saturated and Ar -saturated environments ($\Delta\Delta m$) should correspond adsorbed oxygen [3]. This data is shown for both bare Au and BNNS/Au in Figure 2. Oxygen adsorption is observed from +0.5-0.7 V region, reaching a maximum at +0.5V. The oxygen then desorbs in the ORR potential region, -0.2 - +0.5 V, until the mass of adsorbed oxygen returns to its initial mass at -0.2 V. Alternatively, oxygen absorption occurs more gradually and at potentials higher than +0.7 V on BNNS/Au. However, after the mass of adsorbed oxygen reaches a peak at approximately +0.5V, oxygen appears to rapidly desorb from BNNS/Au reaching a plateau at approximately +0.1V. This indicates that oxygen is adsorbing and desorbing from BNNS/Au at higher potentials than bare Au, which further reinforces the hypothesis that oxygen adsorption/desorption is the key to the kinetics of the BNNS/Au catalytic pathway.

Another key difference between the eQCM measurements taken from bare Au and BNNS/Au is shown in Figure 3. The appearance of an oxidation peak in the CV for BNNS/Au at a potential of approximately +0.3V. This oxidation peak was also associated with a large mass desorption from the BNNS/Au surface as compared to the bare Au surface, shown on the right y-axis of Figure 3 ($\Delta\Delta m_{\text{BNNS-Bare}}$).

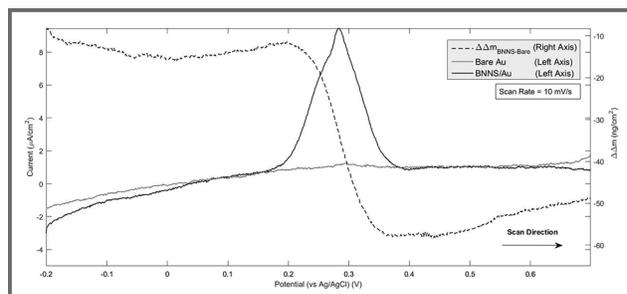


Figure 3: Oxidation sweeps (solid lines) for bare Au and BNNS/Au and difference in adsorbed mass, $\Delta\Delta m_{\text{BNNS-Bare}}$ (right axis).

This desorbing species may be hydrogen desorbing from the surface, which would indicate early onset hydrogen adsorption/desorption. This hypothesis is supported by previous observations that BNNS/Au also enhances the hydrogen evolution reaction (HER).

Conclusion and Future Work:

While further research must be performed to confirm the hypothesis that O_2 is adsorbing/desorbing at higher potentials on BNNS/Au than bare Au, this project has confirmed that a major difference between the kinetics of bare Au and BNNS/Au electrodes is the behavior of O_2 in the ORR potential region. The discovery of the oxidation peak and the corresponding mass desorption occurring on BNNS/Au indicates a potential enhancement of the HER on BNNS/Au. Future studies should aim to determine the absolute difference in oxygen adsorption on BNNS/Au compared to bare Au, as well as the identity of the desorbing species associated with the oxidation peak.

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References:

- [1] Elumalai, G. et al; Phys.Chem.Chem.Phys.; 16, 13755-13761; (2014).
- [2] Sauerbrey, G.; Z. Phys.; 155 (2), 206-222; (1959).
- [3] Tong, S., et al.; Electrochemistry Communications; 34, 33-36; (2013).