Transmission Electron Microscopy (TEM) Studies on Nickel and Molybdenum Nitrides as Oxygen Reduction Reaction Catalysts

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As a promising technology towards efficiently producing electricity for transportation applications, proton-exchange membrane fuel cells (PEMFC) with platinum-based catalysts are limited by the high cost from deploying these precious metals.[1] Developing active, stable and low-cost catalysts has thus become necessary for viable application of PEMFC. Among promising non-precious group catalytic materials for the oxygen reduction reaction (ORR), transition metal nitrides have attracted attention because of their activity and stability in acid electrolyte.[2,3] In the present study, nickel nitride (Ni_xN) and molybdenum nitride (Mo_xN) thin films were prepared by reactive sputtering. These materials were found to be active, stable and selective to reactions, and the properties were found to be dependent on the catalyst structures.

Conventional cross-sectional TEM specimens were prepared to understand better the relationship between the activity and structure. High resolution (HR) TEM images and selected area diffraction patterns (SADP) were taken in a FEI Titan Environment TEM operated at 300kV. As shown in Figure 1A, the cross-sectional TEM image of the Ni_xN thin film has a pillar morphology. SADPs were used to determine the crystal structure at the surface and in the bulk shown in Figure 1B, C respectively. The positions of the SA aperture are marked in 1A. In Figure 1B, the SADP is showing a good match with the diffraction pattern of the Ni_4N cubic structure taken near the $[\bar{2}33]$ zone axis. In Figure 1C, the diffraction rings corresponding to Ni_4N (labeled in red) and Ni_3N (labeled in yellow) are showing up together indicating that the film is primarily composed of Ni_4N, with a minor phase of Ni_3N. The thin film is polycrystalline as seen from the SADP pattern in 1C and HR-TEM images shown in Figure 2.

The electrochemical failure mechanisms of Mo_xN thin films were confirmed through *ex situ* cross-sectional TEM characterization. As seen from Figure 3A and 3B, the thin film has lost a significant amount of the material after an electrochemical test in acidic testing conditions (cyclic voltammograms in 0.1 M $HClO_4$). The bulk thin film is found to be polycrystalline according to the diffraction patterns in Figure 3C. The SADP is showing that the structure of these thin films fits a rocksalt structure with lattice constant of 0.419 nm, which corresponds to MoN with the NaCl structure. In conclusion, the failure mechanism of this thin film was confirmed to be material loss in an acid environment rather than by a phase change by comparing the SADPs and bright-field (BF) TEM from both before and after test thin films.

This work shows the usefulness of TEM characterization to reveal changes in catalytic thin film structures after electrochemical testing in a harsh environment. [4]

References:
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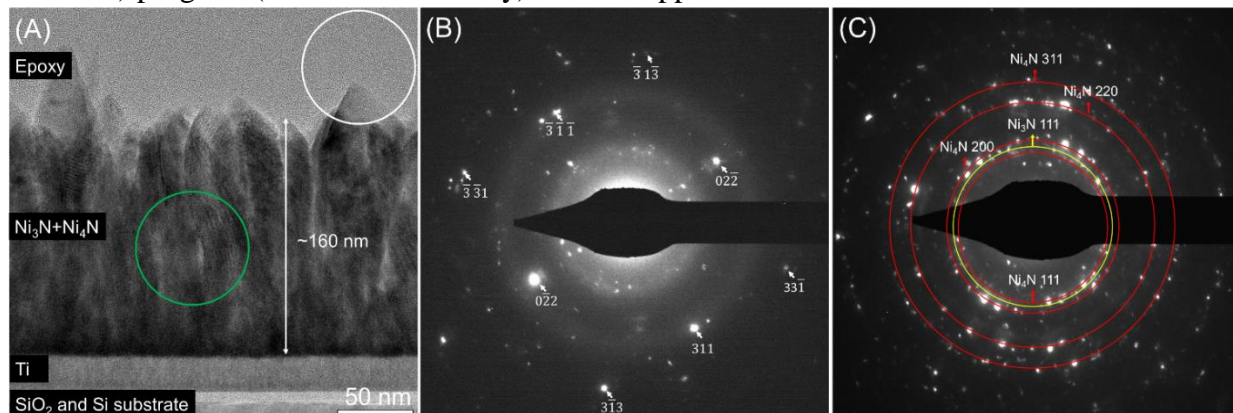
**Figure 1.** BF-TEM and SADP of as-prepared Ni_xN thin films with desired thickness of ~ 160 nm. (A) cross-sectional view, (B) SADP taken from white-circled region in (A) matching DP of Ni_4N from $[\bar{2}33]$ zone axis, (C) SADP taken from green-circled region in (A) showing diffraction rings of Ni_4N and Ni_3N.
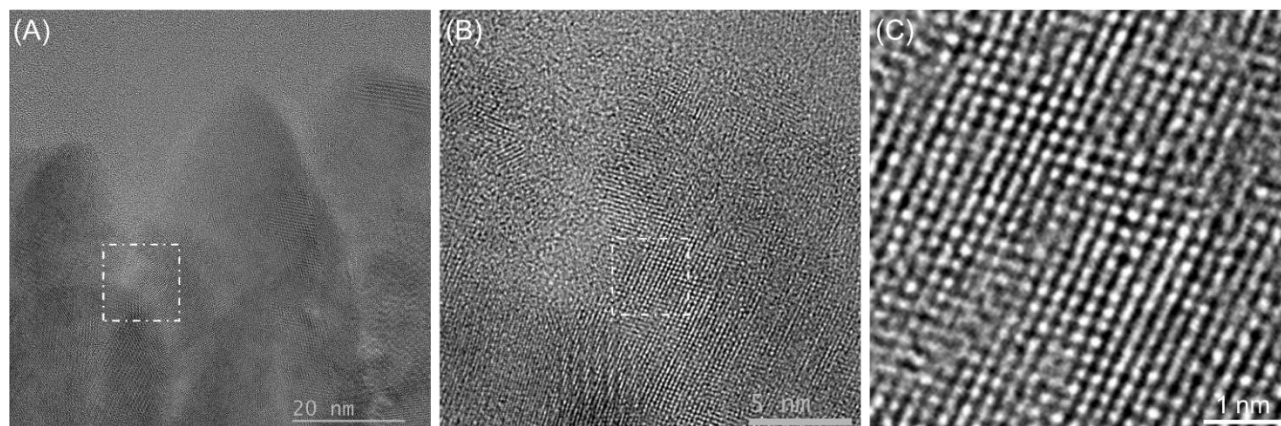
Figure 2. HR-TEM images of the Ni_xN thin film. (A) HR-TEM images of the thin film, (B) magnified image of the marked region in (A) showing lattice fringes. (C) higher magnification of marked box in (B).
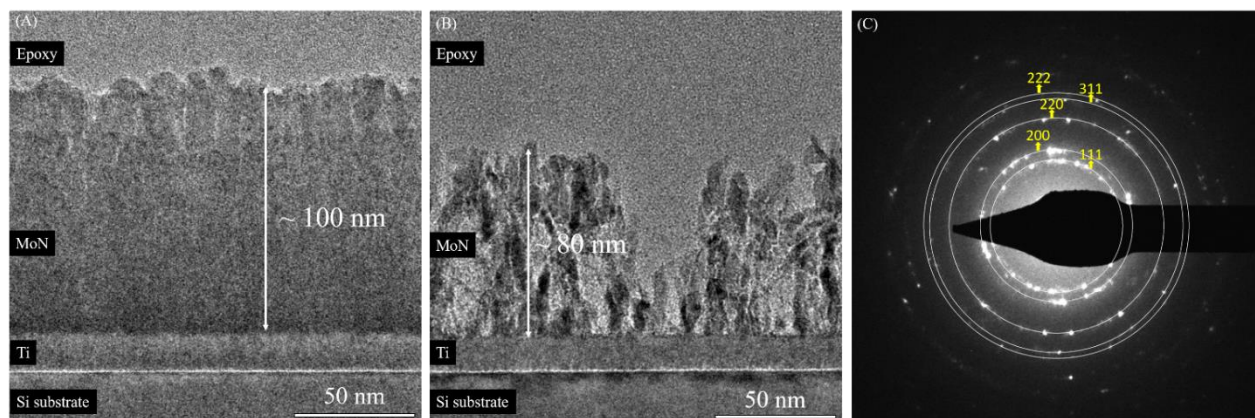
Figure 3. BF-TEM and SADP of Mo_xN thin films. (A) and (B) TEM images of as-deposited and after test Mo_xN thin film showing that the thickness of the film decreased from 100 nm to 80 nm with severe depressions (C) SADP of as-deposited Mo_xN thin film taken over its bulk region showing an FCC pattern consistent with the rocksalt MoN crystal structure both before and after test.