Niobium Oxides as Cathode Electrocatalysts for Platinum-free Polymer Electrolyte Fuel Cells

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Niobium oxides are shown to exhibit oxygen reduction reaction (ORR) activity with high onset potential (ca. 0.85 V vs. NHE) comparable to that for Pt-based catalysts along with excellent stability under acidic conditions.

Polymer electrolyte fuel cells (PEFCs) have attracted considerable attention as a clean power source for electronic devices and are also promising for use in fuel cell vehicles (FCVs) and residential cogeneration systems.[1] However, a major obstacle preventing the widespread commercialization of PEFCs is the high consumption of Pt and related materials as electrocatalysts, which are limited natural resources.[2,3] The commercialization of PEFCs is dependent on the discovery of suitable electrocatalysts based on naturally abundant elements.

A number of transition-metal oxide and oxynitride compounds have relatively high activities as cathode electrocatalysts,[2–8] and transition-metal oxynitrides such as TaO_xN_y and ZrO_xN_y have recently been demonstrated to reduce oxygen at a high onset potential of ca. 0.8 V vs. NHE (normal hydrogen electrode).[4,5] Oxides such as TiO_x and ZrO_x have also been found to exhibit ORR activity.[7,8] As high onset potential is essential in PEFCs in order to ensure small voltage loss at the cathode, these oxide and oxynitride materials are potentially applicable as electrocatalysts in PEFCs in place of existing Pt-based electrocatalysts.

In the present study, niobium oxide is demonstrated to be an effective cathode electrocatalyst with low solubility under acidic conditions. The ORR activities of three niobium oxides (Nb_2O_5, NbO_2, and NbO) are examined, and structural factors affecting ORR activity are investigated.

Nb_2O_5, NbO_2, and NbO were purchased from Kanto Chemical, Strem Chem, and CBMM, respectively, and used as received. A small amount of the oxide (50 mg) was dispersed with 5 mg of carbon black (Vulcan XC-72R) in a mixture of acetylacetone (2.4 mL) and 5 wt % Nafion/isopropanol (0.6 mL). A 50-μL aliquot of the suspension was then dropped onto graphite paper ($1 \times 1\,cm^2$; TGP-H-120, Toray) and then dried at 393 K in air. Electrochemical measurements were performed in aqueous 0.1 M H_2SO_4 solution at room temperature with an Ag/AgCl reference electrode and graphite paper counter electrode. After bubbling with Ar to remove dissolved O_2 for 30 min, oxidation and reduction cycles were repeated between 0.05 and 1.2 V vs. NHE at a scan rate of $5\,mV\,s^{-1}$. A total of 10 cycles was performed in order to ensure the sample electrode had stabilized. Linear sweep voltammograms were recorded after bubbling with Ar or O_2 gas for 30 min.

Neither Nb_2O_5, which is the most stable of the niobium oxides, nor NbO, which is the most reduced state of niobium oxides, displayed activities for ORR. However, NbO_2 exhibited remarkable ORR activity, as indicated by the voltammograms shown in Figure 1. Cathodic current indicative of ORR appears at 0.85 V vs. NHE. Commercial Pt/carbon black catalysts become active for ORR at 1.0 to 0.95 V vs. NHE. The difference in over-potential between NbO_2 and the commercial Pt catalyst is, therefore, only 0.10 V, and it can be expected that the performance of NbO_2-based catalysts will approach that of the Pt-based catalysts with further refinement.

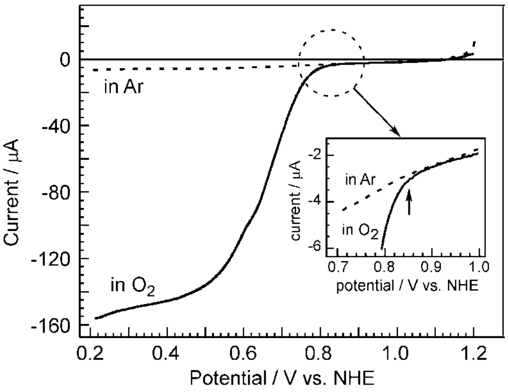

Figure 1. Potential–current curve for NbO_2 powder under Ar and O_2 atmospheres in 0.1 M H_2SO_4. Sweep rate was $5\,mV\,s^{-1}$.

The stability of NbO_2 under acidic conditions was also investigated. NbO_2 powder or Pt black (Aldrich) powder was immersed in aqueous 0.1 M H_2SO_4 solution at room temperature, and after 24 h the leaching of metal ions into the filtrate was evaluated by inductively coupled plasma mass spectroscopy (ICP-MS). The measured solubility of Pt black was 0.38 $\mu mol\,L^{-1}$, consistent with previous reports.[2,3,7] However, NbO_2 was considerably more tolerant of strong acid as measured as 0.05 $\mu mol\,L^{-1}$. Niobium oxides are known to be stable under passivation treatment.[9] X-ray photoelectron spectroscopy (XPS) reveals that the surface of NbO_2 consists predominantly of Nb^{5+} ions (87%).[11] NbO_2 is, therefore, considered sufficiently stable for use under the acidic conditions in a PEFC.

To clarify the origin of the ORR activity exhibited by the Nb-based catalyst, thin films of NbO_x were prepared on glassy carbon plates ($10 \times 10\,mm^2$) by reactive radio-frequency (RF) magnetron sputtering from an Nb metal plate under various partial pressures of O_2. Sputtering was performed for 30 min at 100-W RF power with the substrate maintained at 723 K. The Ar partial pressure in the sputtering chamber was maintained at 8×10^{-2} Pa. Sputtering ensures good electric contact between the NbO_x films and the carbon substrates, eliminating the effect of irregular electric contact in the case of NbO_x powders on the graphite paper. The thickness of the thin films thus prepared is estimated to be ca. 1 μm based on scanning electron microscopy (SEM) observations. The X-ray diffraction (XRD) patterns of the NbO_x films are shown in Figure 2. The crystalline structures of these thin films vary with increasing O_2 partial pressure, from

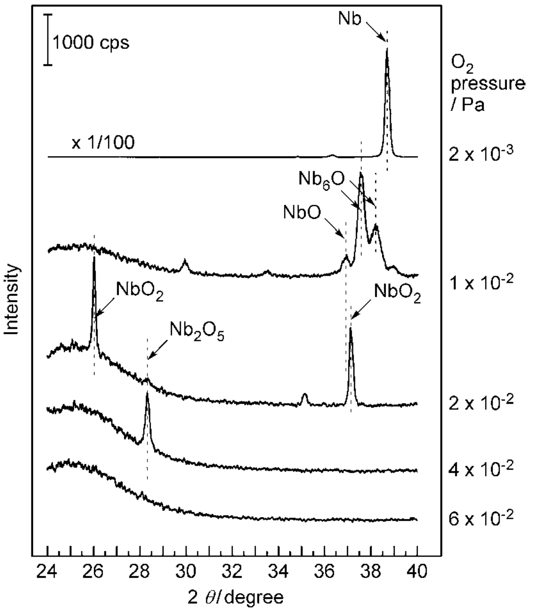

Figure 2. XRD patterns of sputtered NbO_x films prepared at various O_2 partial pressures.

Nb metal to Nb_2O_5. At O_2 partial pressures of 1×10^{-2} to 4×10^{-2} Pa, the samples change structure from Nb_6O–NbO,[10] to NbO_2 and Nb_2O_5. The film prepared at the highest O_2 pressure was amorphous and is speculated to consist of amorphous Nb_2O_5. XPS, however, reveals only Nb^{5+} species on the surfaces of the NbO_2 and Nb_2O_5 films.

Voltammograms of these film electrodes under O_2 are shown in Figure 3. The sample prepared at the lowest O_2 partial pressure produces no ORR current. Samples displaying NbO_2 and Nb_2O_5 XRD patterns, however, produce significant ORR current. The highest potential for ORR, ca. 0.70 V vs. NHE, was obtained for the most oxidized thin film, which had an amorphous structure. In the case of electrodes prepared from powder catalysts, only the NbO_2 powder produced ORR current. However, the results obtained for the sputtered NbO_x films clearly indicate that the bulk structure of NbO_x is not relevant to the appearance of ORR activity. Rather, the production of ORR current appears to be dependent on the formation of a particular surface structure, which can form on NbO_2, Nb_2O_5, and amorphous Nb_2O_5. The lack of observed ORR current for the Nb_2O_5 and NbO powders thus appears to be attributable to inadequate electrical contact between the powder particles and the substrate. The NbO_2 powders are considered to provide good electrical contact with the substrate because of the particle shapes or surface properties. The surface of the NbO_2 powder (Figure 1) was also found by XPS to be predominantly covered with Nb^{5+} species, which were considered to form the active sites.

In summary, niobium oxide was demonstrated to exhibit ORR activity with onset reduction potential comparable to that achieved using a Pt-based catalyst. Furthermore, niobium oxide was found to be remarkably stable under acidic conditions, which is a requirement for application in PEFCs. Using NbO_x films sputtered onto glassy carbon plates, it was found that the surface state is more important to achieving ORR activity than the bulk state. The activity was found to be dependent on the presence of Nb^{5+} species, and active surfaces were successfully produced on NbO_2, Nb_2O_5, and amorphous Nb_2O_5 but not on metallic Nb. Future research on Nb-based materials will involve the development of nitrogen-containing materials and refinement of the preparation technique, with the results to be reported in forthcoming papers.

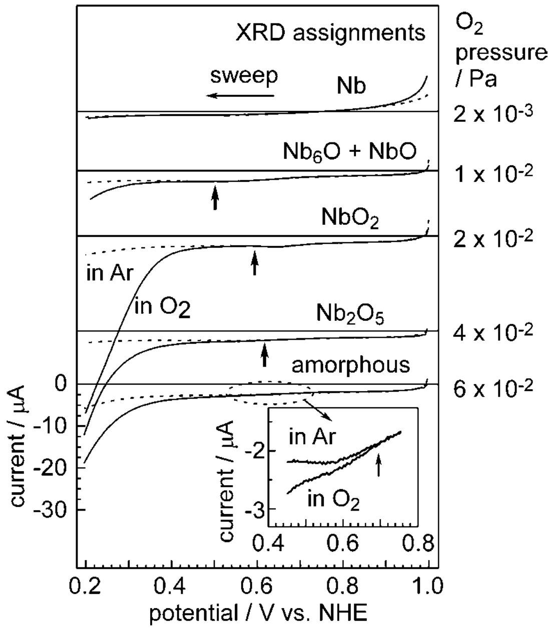

Figure 3. Voltammograms of NbO_x films under Ar and O_2 atmosphere in 0.1 M H_2SO_4. Sweep rate was $5\,mV\,s^{-1}$.

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