Corrosion behavior of mesoporous transition metal nitrides

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ARTICLE INFO

ABSTRACT

Transition metal nitrides (TMN) have many desirable characteristics such as high hardness and good thermal stability under reducing conditions. This work reports an initial survey of the chemical stability of mesoporous TMNs (TM=Nb, V, Cr and Ti) in water at 80 °C at neutral, acidic and alkaline pH. The mesoporous TMNs had specific surface areas of 25–60 m^2/g with average pore sizes ranging from 10 to 50 nm. The high surface areas of these materials enhance the rate of corrosion per unit mass over that of a bulk material, making detection of corrosion much easier. The products were characterized by Rietveld refinement of powder X-ray diffraction (PXRD) patterns and by scanning electron microscopy (SEM). Several nitrides have corrosion rates that are, within error, not distinguishable from zero (± 1 Å/day). Of the nitrides examined, CrN appears to be the most corrosion resistant under acidic conditions. None of the nitrides studied are corrosion resistant under alkaline conditions.

1. Introduction

Transition Metal Nitrides (TMNs) are used in a wide variety of applications due to their unique properties as metallic ceramics [1–4]. TMNs are hard and relatively corrosion resistant as well as electrically conductive [5–7]. These materials have been used in optical coatings, cutting and grinding tools, electrical contacts and catalysts [8–10]. Many of these applications depend on the stability of TMNs under harsh conditions, such as in acidic or alkaline environments, high temperature, high current density, or high electrochemical potential environments.

TMNs are reported to have good electrocatalytic properties for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) and are widely used in electronic devices [11–14]. Therefore, the long-term stability of TMNs in electrolytes is important. Furthermore, studies report that TiN is both electrochemically stable and corrosion resistant in 0.5 M H_2SO_4 up to +0.6 V vs. saturated calomel electrode (SCE) [15]. A similar study done on MoN on Ti substrates showed that MoN was electrochemically stable within the range of 0 to +0.67 V vs. reversible hydrogen electrode (RHE). However, the MoN was not corrosion resistant in H_2SO_4 [16]. Therefore, further studies of the stability of TMNs may suggest even more applications of these unique materials.

Recently, we studied the potential application of nano-structured TMNs in proton exchange membrane (PEM) fuel cells. We have demonstrated the preparation of mesoporous TMNs (pores typically between 10 and 50 nm) by the ammonolysis of Cd, K or Zn containing transition metal oxides above 450 °C [17–19]. These mesoporous materials result from the condensation of atomic scale voids created by the reduction and subsequent volatilization of Cd or Zn, replacement of three O atoms by two N atoms, and the partial reduction of the transition metal oxide to a nitride. Chemical analysis shows that these TMNs retain up to 5–10 mol% of oxygen. Here we report initial studies of corrosion rates of these mesoporous nitrides at 80 °C, when exposed to acidic or alkaline aqueous solutions, since several different types of PEM fuel cells are typically run under these conditions.

Corrosion refers to the gradual destruction of a material by chemical reaction with its environment. Relevant chemical reactions are typically oxidation/reduction, hydrolysis, dissolution, and/or metathesis. The specific environmental conditions are critical in determining the corrosion behavior (or lack thereof). Most relevant are ambient conditions (typically for storage or idle periods), working conditions, or accelerated testing conditions [20]. Accelerated testing is usually performed at temperatures above those of typical working conditions, since the rates of most reactions increase with increasing temperature. Of course, the presence of liquids or liquid films, especially of water, dissolved species, pH, etc., as well as the presence of air (oxygen and perhaps trace gasses of organic substances), may also be critical to understanding the observed behavior.

Assuming that the rate of corrosion is proportional to the surface area exposed to a specific environment, we expect that

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the detection of corrosion of these mesoporous nitrides (BET specific surface area 25–60 m^2/g) would produce a higher mole fraction of corrosion products in a given time than would be observed in bulk samples. Thus, detection of slow corrosion processes in mesoporous systems is easier and more sensitive. Here, we report the corrosion behavior of these mesoporous metal nitrides exposed to acidic and alkaline solutions at 80 °C (or for CrN also at 150 °C) for 2 weeks.

2. Methods

Mesoporous TMN (TM=Nb, V, Cr and Ti) were made by ammonolysis, a process we recently reported (see Supplementary material)[17]. Similar conditions as previously reported were used for syntheses of the mesoporous TMNs as summarized in Table 1. Several different stock solutions were prepared for use in the corrosion studies: (H$_2$O, 2 M solutions of NaOH, HCl, HNO$_3$ and H$_2$SO$_4$). About 100 mg of TMN was added to a 5 ml glass container, 3 ml of the stock solution was added, and the container sealed by screwing on a Teflon lined cap. Typically the container was heated to 80 °C for 2 weeks and then the contents characterized. In some cases, a Teflon lined Parr bomb was used for reactions with NaOH to avoid reaction of the base with SiO$_2$ or for reactions at temperatures up to 150 °C to examine the behavior under harsher conditions. After heating, any remaining solid products were washed by deionized water and dried at room temperature on a vacuum line for 24 h.

The initial and any remaining powders after reaction were examined with a Rigaku Ultima VI powder X-ray diffractometer (PXRD) with Cu $K\alpha$ radiation ($K\alpha_1$, $\lambda=1.5406$ Å and $K\alpha_2$, $\lambda=1.5444$ Å). Crystal structures of the oxides and resultant nitrides were confirmed by PXRD profiles using the GSAS package [21]. The crystalline domain sizes of TMNs can be estimated from a Rietveld fit of the Lorentzian function, as discussed previously [17]. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a LEO-1550 field emission SEM (FSEM). The BET specific surface areas were measured at -196 °C using a Micromeritics ASAP 2020 system. The samples were degassed at 200 °C for 24 h on a vacuum line prior to BET measurement.

Corrosion can result in insoluble amorphous or crystalline solid products, or in soluble products. Insoluble crystalline products are easily detected by PXRD when they are greater than about 5 mol% of the final product. SEM imaging can be even more sensitive, if the morphology of the corrosion product is quite different than that of the initial material. Insoluble amorphous products may be more difficult to detect or quantify, especially if the corrosion is topotactic. In that case, only large amounts of corrosion would be detectable by PXRD as the signal from the remaining nitride would significantly decrease. Of course, if the amorphous product has different morphology than the mesoporous nitride, it will be detectable by SEM. Finally, soluble products may be

detectable by forming a colored supernatant above any remaining solid or by significant mass loss of the remaining solid product. Again, significant corrosion of this type would be expected to completely dissolve the nitride. For example, we observed the complete dissolution of VN in nitric acid to a green solution (vide infra).

In these mesoporous nitrides the crystalline domain sizes are only slightly smaller than the wall thickness of the mesoporous nitride. Thus, to a good approximation (within a factor of 2 or so) is that all domains are exposed to the environment. If we assume that corrosion occurs at approximately at the same rate at all surfaces, we can estimate the corrosion rate from the decrease in domain size after the reaction. Assuming a simple linear rate equation, we can estimate the corrosion rate using the equation below:

$$Rate = \frac{(d_o - d_p) \times 0.5}{Time} \qquad (1)$$

d_o and d_p are the calculated average domain crystalline size of the product and the original sample, respectively. We report the corrosion rate in units of Å/day. As we will see, this method allows one to observe rates as low as 1 Å/day. Faster corrosion rates, up to 15 Å/day, are easily determined in a 2-week reaction. Shorter reaction times would of course allow quantification of faster rates, but quantifying higher rates is not of interest here.

3. Results

Before corrosion testing, the mesoporous TMNs were analyzed by PXRD, BET and SEM. All the TMNs have high specific surface area and mesoporous features. The TMNs were then examined after heating in the above separate solutions. The samples were heated all in one oil bath on an electronic hot plate and kept at 80 °C for 2 weeks. Following the test, any remaining solid products were washed with deionised water and dried in a desiccator. Finally, the dried corrosion products were analyzed again by PXRD and SEM.

3.1. Mesoporous NbN

The mesoporous NbN is a black powder. After treatment, all but one of the NbN samples remained a black powder and all the supernatants remained colorless and clear. However, treatment in NaOH resulted in a visible, thin, white powder layer coating the
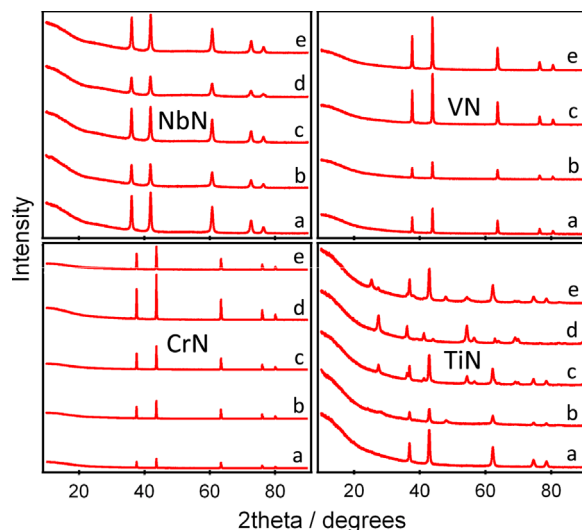
Table 1
Summary of ammonolysis conditions, refined lattice parameters and calculated domain size of mesoporous TMNs: reactions are at an ammonia flow rate of 200 cm^3 min^{-1}. All TMN (TM=Nb, V, Cr and Ti) crystallized in space group $Fm\bar{3}m$ Units for temperature and reaction time are degree Celsius (ºC) and hour (h), respectively.

TMN	NbN	VN	CrN	TiN
Precursor	Zn$_3$Nb$_2$O$_8$	Zn$_3$V$_2$O$_8$	ZnCr$_2$O$_4$	Zn$_2$TiO$_4$
Condition	700 ºC, 24 h	500 ºC, 8 h	800 ºC, 16 h	800 ºC, 16 h
a (Å)	4.3218(1)	4.1271(1)	4.1430(1)	4.2189(1)
Domain size (nm)	23	35	31	28
BET surface area (m^2/g)	26.6 ± 0.1	59.1 ± 0.1	45.1 ± 0.1	27.3 ± 0.1
C value	154.3	102.7	154.4	197.6
Micropore volume (cm^3/g)	1.6 × 10^{-3}	0.1 × 10^{-3}	0.9 × 10^{-3}	2.3 × 10^{-3}
Micropore area (m^2/g)	4.1	1.3	2.2	5.6

Fig. 1. PXRD patterns of MN (M=Nb, V, Cr and Ti) after the treatment at 80 °C for 2 weeks in H$_2$O (a), 2 M of NaOH (b), HCl (c), HNO$_3$ (d) and H$_2$SO$_4$ (e).