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Pseudocapacitive charge storage via hydrogen insertion for molybdenum nitrides

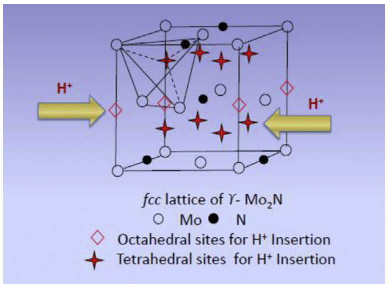
Priyanka Pande [a], Aniruddha Deb [b], Alice E.S. Sleightholme [a], Abdoulaye Djire [a], Paul G. Rasmussen [a, b, c], James Penner-Hahn [b], Levi T. Thompson [a, c, d, *]

[a] *Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA*
[b] *Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA*
[c] *Hydrogen Energy Technology Laboratory, University of Michigan, Ann Arbor, MI 48109-2136, USA*
[d] *Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109-2316, USA*

HIGHLIGHTS

- Proton insertion into interstitial sites linked to pseudocapacitive charge storage.
- *In situ* X-ray absorption spectra track reversible changes in Mo_2N on cycling.
- Theoretical capacitance for Mo_2N exceeds 1500 F/g on interstitial site occupation.

GRAPHICAL ABSTRACT



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ABSTRACT

Early transition metal nitrides are promising materials for use in electrochemical capacitors and as electrocatalysts due to their high electronic conductivities, high surface areas and electrochemical stabilities. In addition to double-layer (electrostatic) charge storage, these materials store charge via a pseudocapacitive mechanism involving charge-transfer reactions. This paper describes electrochemical and *in-situ* X-ray absorption spectroscopic results that provide important insights regarding the pseudocapacitive charge storage mechanism for molybdenum nitrides in aqueous acids. From analysis of the rest potentials at varying pH values, we concluded that electrons and protons were coupled during charge transfer with a ratio of ~2 electrons per proton. Cycling the Mo_2N electrodes between −0.73 and −0.19 V, the stability window for this material, resulted in the removal of approximately one electron per Mo from a band that was primarily Mo in character. The extended X-ray absorption fine structure spectra indicated minimal changes in the immediate local structure around Mo as the potential was varied. The results are consistent with reversible hydrogen insertion into and extraction from interstitial sites in the Mo_2N lattice. Charge storage capacitances in excess of 1500 Fg^{-1} are predicted for materials with full occupation of these interstitial sites.

1. Introduction

Molybdenum nitrides, like other early transition metal nitrides and carbides, belong to a class of materials called interstitial

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* Corresponding author. Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA.
E-mail address: ltt@umich.edu (L.T. Thompson).

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compounds [1,2]. These materials are characterized by the presence of small atoms like nitrogen and carbon in interstitial sites formed by the metal lattice, and find commercial application in ultrahard coatings [1,2]. Due to their high electronic conductivities, ability to be produced with high surface areas, stability in a variety of electrolytes and high specific capacitances, early transition metal nitrides have also attracted attention for use as catalysts and electrocatalysts [2–8] and in electrochemical capacitors [9–13] Dimolybdenum nitride (Mo_2N), for example, can have capacitances in excess of 300 Fg^{-1} in sulfuric acid (H_2SO_4) [13] and vanadium nitride (VN) has been reported to possess capacitances in excess of 1300 Fg^{-1} in aqueous potassium hydroxide (KOH) [11]. These capacitances exceed the purely double-layer capacitance values, and have been attributed to pseudocapacitive charge storage. Pseudocapacitive charge storage involves fast, near-surface redox reactions of the electrolyte ions with the electrode material [9–13] and has been reported to contribute to the high specific capacitances of Ru [14,15] and Mn oxides [16,17].

Research described in this paper aimed to enhance our understanding of the charge-storage characteristics for γ-Mo_2N in aqueous H_2SO_4 with a particular focus on defining the pseudocapacitive mechanism. A key hypothesis for this research was that the pseudocapacitance derived from the insertion of protons into the γ-Mo_2N lattice. Previously we reported that the active electrolyte species for γ-Mo_2N in H_2SO_4 was H^+ based on results from electrolyte ion-substitution and isolation experiments [13]. Here we describe results from rest potential measurements and *in-situ* X-ray absorption spectroscopy (XAS) which allowed us to track changes in the electronic and bonding character of the γ-Mo_2N based electrode as it was electrochemically cycled. A half-cell reaction is proposed that describes the charge-storage mechanism for this material in H_2SO_4. This result will not only benefit efforts to develop high energy electrochemical capacitors based on early transition metal nitrides but also enhance our understanding of characteristics contributing to their electrocatalytic and catalytic properties.

2. Methods

The material was synthesized using a temperature programmed reaction of $(NH_4)_6Mo_7O_{24}.4H_2O$ with anhydrous NH_3 gas [11–13]. The material was characterized by X-ray diffraction and the surface area was measured by nitrogen physisorption using the Brunauer–Emmett–Teller (BET) method. Details regarding the synthesis procedure and the results for physical characterization are described in the Supporting information, as are the methods for the preparation of electrodes and electrolyte solutions.

Prior to the rest-potential measurements, the pH of each of the various H_2SO_4 solutions was measured using an Accumet BioBasic pH-meter with Ag|AgCl electrode. Rest-potential measurements were performed using an Autolab PGSTAT302N potentiostat/galvanostat (Metrohm, U.S.). A three-chamber quartz cell was used to perform these measurements. A Pt foil was used as the counter electrode and Hg|HgSO$_4$ (Sat. K_2SO_4, Radiometer Analytical) was used as reference electrode. The electrolyte solutions were deaerated with N_2 (99.998% with an oxygen trap) for at least 20 min before the experiments. A N_2 blanket was maintained during the measurements. Chronopotentiometry experiments at zero applied current were performed as the voltage (V) was recorded as a function of time (t). The experiments were continued until $dV/dt \leq 10^{-5}$ V s^{-1}; the potential beyond this point was considered to be the rest potential.

The *in-situ* XAS measurements were performed using the electrochemical reaction cell shown in Fig. A3 (Supporting information). Pt black (Alfa Aesar) coated Ti foil (99.7%, Aldrich) was used as a counter electrode and a Pt wire was used as a quasi reference electrode. The measurements were performed in an aqueous solution of 0.1 mol dm^{-3} H_2SO_4. Celgard 3501 was used as the separator. The electrolyte solution was deaerated with N_2 (99.998% with an oxygen trap) for at least 20 min before addition into the cell. After the electrolyte solution was added the cell was sealed.

The XAS measurements were performed in transmission mode at the bending magnet beam line station D of the DND-CAT (Sector 5) at the Advanced Photon Source (APS). A water cooled Si(111) double-crystal monochromator was used for energy selection, and incident and transmitted X-ray intensities were measured using Ar filled ion chambers at 1 atm pressure with an applied voltage of 300 V. The beam size was defined as 1×3 mm^2 using slits and had an incident photon flux of ~10^{10} photons s^{-1}.

Before adding the electrolyte solution, XAS measurements were made on the “as-is” sample. The deaerated electrolyte solution was then added and the cell was sealed. Cyclic voltammograms were acquired using a CH-instruments CH-600D potentiostat. The scan rate was 5 mV s^{-1} and the stable-operating voltage range was deter-mined vs. the Pt wire reference electrode. The voltage window was divided into discrete potential steps as shown in Fig. 2 and *in-situ* XAS measurements were performed at these potentials. The samples were allowed to equilibrate for at least 1000 s at each voltage prior to collecting the XAS spectra. Three scans (19,800–20,980 eV using 5 eV steps in the pre-edge region, 0.5 eV steps in the near-edge region and 0.05 Å^{-1} steps in the EXAFS region) were taken at each applied voltage and averaged for further analysis. The data were integrated for 1 s in the pre-edge, 1.5 s in the near edge region and 1.5–25 s in the EXAFS region for a total scan time of about 2400 s. The energy was calibrated by simultaneously collecting spectra for a Mo foil, with the first inflection point of the Mo foil defined as 20,000 eV. The raw data were converted into extended X-ray absorption fine structure (EXAFS) spectra using ATHENA [18], with E_0 defined as 20,000 eV, and a cubic spline used to remove the EXAFS background. The resulting $\chi(k)$ function was weighted with k^3 to account for the damping of oscillations with increasing k. The radial structure functions presented here were obtained by Fourier transformation of k^3 $\chi(k)$ using a k range of 1.5–15 Å^{-1}.

Data were fit using IFFEFIT [18] with *ab initio* amplitude and phase functions calculated using FEFF9.0 [19], and using the crystallographic coordinates for γ-Mo_2N. The nearest-neighbor EXAFS was modeled as a shell of Mo–N at ~2.1 Å, with both the coordination number and the Debye–Waller factor treated as variable parameters. The next-nearest neighbor Mo–Mo shell at ~2.8 Å is significantly smaller than would be expected for an ideal *fcc* structure. This could be modeled either with the coordination number fixed at 12 and a variable Debye–Waller factor, which refined to physically unrealistic values of ~0.028 Å^2, or with the

Table 1
Best fit parameters for Mo_2N EXAFS (k = 2.0–13 Å^{-1}, k^3 weighting, R-range = 1–4 Å). See text for a description of the fits.

Sample	Treatment	Mo–N			Mo–Mo		ΔE_0
		N	R/Å	$\sigma^2 \times 10^3$/Å^2	N	R/Å	
As-is	As-is	1.9	2.11	4.5	1.0	2.86	5.1
Mo_2N-0.19	0.19 V	3.1	2.12	7.6	0.9	2.87	7.2
Mo_2N-0.19[a]	0.19 V[a]	3.2	2.13	7.7	0.9	2.86	7.2
Mo_2N-0.3	0.3 V	3.2	2.11	7.1	0.9	2.85	5.7
Mo_2N-0.3[a]	0.3 V[a]	3.2	2.12	7.1	0.9	2.85	5.8
Mo_2N-0.46	0.46 V	3.6	2.10	7.0	1.0	2.86	3.6
Mo_2N-0.46[a]	0.46 V[a]	3.5	2.10	7.0	1.0	2.85	3.6
Mo_2N-0.73	0.73 V	3.8	2.11	6.9	1.3	2.85	3.0
Mo_2N-0.73[a]	0.73 V[a]	3.8	2.12	6.9	1.3	2.85	3.1

[a] EXAFS measured on reverse cycle of potential.