



Full paper

Pseudocapacitive storage via micropores in high-surface area molybdenum nitrides

Abdoulaye Djire^{a,*}, Jason B. Siegel^b, Olabode Ajenifujah^a, Lilin He^c, Levi T. Thompson^{a,b,d,**}^a Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA^b Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA^c Oak Ridge National Laboratory, TN, USA^d Hydrogen Energy Technology Laboratory, University of Michigan, Ann Arbor, MI 48109-2136, USA

ARTICLE INFO

Keywords:

Supercapacitors
Transition-metal molybdenum nitrides
Pseudocapacitance
Micropores

ABSTRACT

Nanostructured early-transition-metal nitrides possess high capacitances that are consistent with a pseudocapacitive storage mechanism. Prior publications suggest that the mechanism involves the interactions between protons and the metal. This paper describes the use of in-situ small angle neutron scattering as a function of the potential applied to the electrode and *ex-situ* physical and electrochemical techniques to determine specific details regarding the storage mechanism for high-surface-area Mo nitride (γ -Mo₂N) in 0.1 mol dm⁻³ H₂SO₄ electrolyte. The results demonstrate that the pseudocapacitance involves a proton-coupled electron transfer (2e⁻ for every H⁺) via micropores, which is accompanied by the reduction/oxidation of Mo. These results suggest that capacitances in excess of 1500 Fg⁻¹ in 1.2 V could be achieved in aqueous acidic electrolytes.

1. Introduction

High-surface area early transition-metal carbides and nitrides find a variety of applications including use as catalysts and electrocatalysts [1–8], and as electrode materials in electrochemical energy storage devices such as supercapacitors [9–22]. These materials are interstitial compounds in which small non-metal atoms like carbon and nitrogen occupy interstitial sites formed by the metal lattice [1–5], typically possess high electronic conductivities [9–14], and are stable in a variety of aqueous and non-aqueous electrolytes [8–20]. We are particularly interested in the charge storage mechanism for early transition metal nitrides in aqueous electrolytes. Previously it was reported that charge is stored via redox reactions, ion intercalation and/or electrosorption [10–14]. Given the nature of the materials and magnitudes of the capacitances, we speculated that protons are intercalated into the interstitial sites. Research described in this paper, characterized the electronic and physical interactions between γ -Mo₂N and protons in aqueous acidic electrolytes using in-situ small angle neutron scattering (SANS) combined with chronoamperometry, cyclic voltammetry (CV), scanning electron microscopy (SEM), and N₂ physisorption analysis. We exploit the unique sensitivity of neutron scattering to hydrogen, which allows us to track the fate of proton within pores of the materials. Elastic neutron scattering at small scattering angles allows an

interrogation of structures at the nanoscale (i.e. 1–100 nm). In addition to shedding light on the charge storage mechanisms for Mo nitrides, results provided in this paper will benefit efforts to design high-energy density supercapacitors devices based on these materials.

2. Experimental

2.1. Material synthesis

The high-surface-area Mo₂N was prepared from (NH₄)₆Mo₇O₂₄·4H₂O (81–83% as MoO₃, Alfa Aesar) via the temperature-programmed reaction with NH₃ (Cryogenic Gases, 99.999%). Briefly, the solid precursor was supported on a quartz-wool plug in a quartz tube reactor with a flowing stream of NH₃ as the temperature was increased to 700 °C. After synthesis, the material was quenched to room temperature and then exposed to a flowing mixture of 1% O₂/He (Cryogenic Gases, 99.999%) to form an oxygen-rich passivation layer on the surface; this passivation layer prevents bulk oxidation of the material when exposed to air [2–4].

2.2. Physical characterization

The surface areas and pore size distributions of the passivated

* Corresponding author.

** Co-corresponding author.

E-mail addresses: adjire@umich.edu (A. Djire), ltt@umich.edu (L.T. Thompson).

materials were determined by N_2 physisorption using a Micrometrics ASAP 2010 analyzer. The Brunauer-Emmett-Teller (BET) method was used to fit the isotherms and quantify the surface area. The Barrett-Joiner-Helenda (BJH) and Horvath Kawazoe (HK) methods were used to determine the meso- and micropore size distributions, respectively. Prior to analysis, the materials were degassed in vacuum at 350 °C for 24 h. The materials were also characterized by X-ray diffraction (XRD) using a Rigaku Miniflex Diffractometer with $Cu\ K\alpha$ ($\lambda = 0.15404\text{ nm}$) source. The XRD was carried out at a scan rate of $5.0^\circ\text{ min}^{-1}$ with a step size of 0.1° over a 2θ range of $10\text{--}90^\circ$. The JADE 10.0 software was used for peak identification. SEM was used to examine morphologies of the passivated materials. The microscopy was carried out using a FEI Nova 200 Nanolab field emission electron microscope operating at an accelerating potential of 10.0 kV.

2.3. Electrochemical characterization

Electrochemical characterization was carried out using a three-electrode cell (ECC-Aqu, EL-Cell FmbH, Germany) with 0.1 mol dm^{-3} H_2SO_4 electrolyte in H_2O and D_2O solvents. The electrolytes were deaerated with N_2 for 1 h prior to the electrochemical experiments to remove dissolved oxygen. The cell was assembled with an 18 mm diameter, 1.55 mm thick glass fiber separator. A 2.54 cm^2 counter electrode (Kynol activated carbon fabric ACC-507-15, sp. S. A. $1500\text{ m}^2\text{ g}^{-1}$) was used. The working electrode was prepared by mixing the Mo_2N (92 wt%), carbon black (3 wt%), Super PLi (TIMCAL) and polyvinylidene fluoride (5 wt%, Kynar) in N-methylpyrrolidone solvent (Alfa Aesar). The resulting slurry was spread onto a Ti foil and then dried in vacuum at 80 °C for 8 h. The mass of the active material was determined by subtracting the mass of the Ti substrate from the mass of the coated electrode (Ti + active material). Approximately, 3 mg of active material was coated onto the substrate. The working electrode diameter was 16 mm. A Pt wire (1 mm diameter) was used as the quasi-reference electrode. This electrode is electrochemically stable in aqueous electrolytes, and has been successfully used as a quasi-reference electrode under the conditions employed in our investigations [14]. The counter electrode and separator were soaked overnight in the deaerated electrolyte, to ensure proper wetting. The currents and potentials were measured using an Autolab PGSTAT302N potentiostat. Cyclic voltammetry (CV) was used to determine the total capacitance of the material at different scan rates. The specific capacitances, C (Fg^{-1}), were estimated by integrating the area under the cyclic voltammograms according to [23]:

$$C = \frac{\int i dV}{m\nu\Delta V} \quad (1)$$

where i is the current, ΔV is the voltage window, m is the mass of active material and ν is the potential scan rate.

2.4. In-situ SANS characterization

Prior to the in-situ SANS experiments, the working electrode was prepared by welding together 24 electrodes (approximately 1 g of total active material) using Ti wire (0.1 cm by 5 cm). The temperature of the electrodes was within 24–28 °C as indicated by the pyrometer; therefore there was no overheating of the active material. Similar to the electrodes used for CV analysis, the individual electrodes were made by slurry-coating the Mo_2N (same composition as before) onto Ti foil substrates (99.97%, Alfa Aesar, 0.032 mm thickness) and dried in a vacuum oven at 80 °C for 8 h. The Mo_2N coating was $\sim 300\ \mu\text{m}$ thick and covered (on both sides of the Ti foil) an area approximately 0.8 cm wide by 1.5 cm long. A Pt wire (1 mm diameter) and activated carbon (Kynol activated carbon fabric ACC-507-15, sp. S. A. $1500\text{ m}^2\text{ g}^{-1}$) were used as quasi-reference and counter electrodes, respectively, similar to the *ex-situ* electrochemical characterization experiments. A quartz cell (1 cm \times 2 cm wide and 5 cm long) from Hellma Company

was used for the SANS experiments. The cell was sealed using a PTFE lid and vacuum grease seal and mounted on an aluminium stand. The system was demonstrated to be air-tight as an air-sensitive material was stored in it for several days; upon subsequent exposure to air, the material was pyrophoric. The same methodology was applied to the cells used for in-situ SANS experiments. A simplified schematic of the in-situ experimental setup is shown in Fig. S1.

The SANS experiments were conducted at the Oak Ridge National Laboratory (ORNL), using a General Purpose SANS instrument with a neutron wavelength of $\lambda = 4.75\ \text{\AA}$ and a wavelength spread, $\Delta\lambda/\lambda$ of 0.13 [24]. Two sample-to-detector distances, 12 and 0.26 m, were used to cover a q range from $0.005\ \text{\AA}^{-1}$ to $0.9\ \text{\AA}^{-1}$, where q is the scattering vector. The average acquisition time for each scattering curve was ~ 30 min. All the measurements were conducted at room temperature. The raw data was corrected for instrumental background, detector efficiency, and transmission. The corrected 2D data were azimuthally averaged to produce the 1D profile $I(q)$ vs. q , where q is the scattering vector ($q = 4\pi\sin\theta/\lambda$) and 2θ is the scattering angle, and placed on an absolute scale (cm^{-1}) via the use of calibrated standards (e.g. vitreous carbons) [25].

A SANS was collected for the dry sample prior to adding the electrolyte. After adding approximately 10 ml of 0.1 mol dm^{-3} H_2SO_4 in D_2O (deaerated) to the sealed in-situ electrochemical cell, SANS measurements were performed at the open circuit potential (OCP) or rest potential. Note that prior to collecting the SANS data at OCP, the system was allowed to equilibrate for 1 h to ensure complete wetting of the electrodes. The samples were also allowed to equilibrate for at least 30 min at each additional potential prior to collecting the SANS. The cyclic voltammograms were acquired using a CH-instruments CH-600D potentiostat. The scan rate was 1 mV s^{-1} and the stable-operating potential range was defined as the region where the current did not increase rapidly. Escalation of current suggests irreversible parasitic reactions such as H_2 or O_2 evolution reactions, and formation of oxides [23,32]. The in-situ SANS measurements were performed at discrete potentials to monitor changes in the distribution of H^+ as a function of applied potential.

3. Results

3.1. Physical properties

The XRD pattern and pore size distribution for the as-synthesized material are shown in Fig. 1. Peaks in the XRD pattern matched those in the JADE 10.0 software library for γ - Mo_2N , the face-centered cubic polymorph of Mo_2N ; this result confirmed that the bulk material was phase-pure (Fig. 1a) [2–4]. For convenience, this material will be referred to simply as Mo_2N . Line broadening analysis indicated that the average crystallite size was $\sim 5.7 \pm 0.1\text{ nm}$. The pore size distribution indicated the presence of primarily micropores ($< 2\text{ nm}$) and mesopores (2–50 nm). The total surface area and average pore size for this material were $\sim 140 \pm 0.2\text{ m}^2\text{ g}^{-1}$ and $3.7 \pm 0.2\text{ nm}$, respectively. The SEM micrographs indicated that the material is highly porous (Fig. S2), consistent with the adsorption measurements. The high porosity will enhance the scattering intensity [24], thus enabling the direct investigation of adsorbed proton on the Mo_2N material during electrochemical cycling.

3.2. Electrochemical properties

Fig. 2a shows cyclic voltammograms for Mo_2N in aqueous H_2SO_4 electrolytes (H_2O and D_2O solvents). The voltammograms are nearly identical and indicate redox chemistry over $\sim 1.2\text{ V}$. Reversible redox peaks at $-0.95/-0.90\text{ V}$ and $-0.35/-0.30\text{ V}$ from the voltammograms are consistent with faradaic or pseudocapacitive charge storage processes involving fast, near-surface redox reactions of the electrolyte ions with the electrode material [23,29,30]. While the surface oxidation

Download English Version:

<https://daneshyari.com/en/article/7952301>

Download Persian Version:

<https://daneshyari.com/article/7952301>

[Daneshyari.com](https://daneshyari.com)