



Short communication

Charge storage on nanostructured early transition metal nitrides and carbides

Priyanka Pande^a, Paul G. Rasmussen^a, Levi T. Thompson^{a,b,*}^a Department of Chemical Engineering, University of Michigan, Ann Arbor 48109-2136, USA^b Department of Mechanical Engineering, University of Michigan, Ann Arbor 48109-2136, USA

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ABSTRACT

Phase pure, nanostructured V, Mo and W nitrides and carbides were synthesized and characterized in aqueous KOH and H₂SO₄ electrolytes. Capacitances for most of the materials exceeded that expected for double layer charging and suggested a pseudocapacitive storage mechanism. With the exception of β-Mo₂C, the materials were stable in KOH and/or H₂SO₄ electrolytes. Capacitances for VN in KOH and γ-Mo₂N in H₂SO₄ were the highest and exceeded 200 F g⁻¹. The charge-storage species were interrogated using an ion isolation method. The results provide unambiguous evidence that OH⁻ was the principal charge storage species responsible for the pseudocapacitance demonstrated for VN in KOH while H⁺ was the principal species for γ-Mo₂N in H₂SO₄.

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1. Introduction

Batteries are the principal devices used for commercial and military energy-storage applications. While these devices can have energy densities exceeding 100 Wh kg⁻¹, this energy is difficult to fully access in pulsed and high power applications due to the relatively slow kinetics associated with their redox processes. Electrochemical capacitors could complement batteries for applications including load-leveling and uninterruptible power supplies [1]. In terms of their specific energy and power, they fill the gap between conventional capacitors and batteries. These devices can be included in hybrid configurations to manage short, high power pulses, thereby minimizing stresses on the primary energy-storage devices [1,2].

Electrochemical capacitors (ECs) store charge in the electrochemical double-layer that is produced by electrostatic separation of electrolyte ions at the electrode–electrolyte interface and for some materials by pseudocapacitive mechanisms involving fast, near-surface redox reactions [3]. Commercially available ECs are based on double-layer capacitance and consist of high surface area carbon electrodes with organic electrolytes [4–6]. The capacitances for these materials are typically 100–125 F g⁻¹ and energy densities for the corresponding devices can reach 5 Wh kg⁻¹ [4,5]. The charge stored in carbon-electrodes can be limited as most of the

surface area is derived from micropores that are smaller than the solvated electrolyte ions [3,4].

A number of pseudocapacitive materials have been reported including conducting polymers like polyaniline, polypyrrole, polythiophene and their derivatives [7,8] and the oxides of Ru, and Mn [3,9–13]. Hydrrous RuO₂ is the benchmark pseudocapacitive material with reports of capacitances up to 1300 F g⁻¹, depending on the charge–discharge conditions [3,9] and energy densities in excess of 8 Wh kg⁻¹ [3], however, the high cost of Ru limits its large-scale use. MnO₂ is a lower cost alternate to RuO₂, but has a lower electronic conductivity [4] and the capacitances for MnO₂ powders or micrometer-thick films are typically in the range of 150–220 F g⁻¹ [2]. Ultra-thin MnO₂ films formed on metal current collectors have been reported to have capacitances near 1000 F g⁻¹ [12,13]. Due to the very low loadings, thin films are limited to micro-system applications and are not suitable for large-scale industrial applications [12].

Early transition metal nitrides have been reported to exhibit pseudocapacitive behavior in aqueous electrolytes [14–16]. These materials have high electronic conductivities [21], are stable in aqueous electrolytes [14–16] and can be synthesized with high surface areas [17–22]. Vanadium mononitride (VN) has been the most studied for supercapacitor applications [14,15]. The highest capacitance reported for VN is 1340 F g⁻¹ [16], however, the charge storage mechanism for these materials is not well understood. Kumta et al. used results from post-cycling infrared and X-ray photoelectron spectroscopic characterization to propose that the charge mechanism for VN in aqueous KOH electrolyte involved a redox reaction of the oxy-nitride passivation layer with OH⁻ as well as double-layer charging [16]. Conway et al. suggested

* Corresponding author at: Department of Chemical Engineering, University of Michigan, Ann Arbor 48109-2136, USA. Tel.: +1 734 936 2015; fax: +1 734 763 0459.
E-mail address: ltt@umich.edu (L.T. Thompson).

two reactions to account for charge storage for Mo₂N in aqueous H₂SO₄ electrolytes: the first involving protons with the reduction of Mo and the second an oxy/hydroxy redox couple involving the hydrolyzed Mo [14].

Results described in this paper unambiguously define the species involved in charge storage for high surface area V, Mo and W nitrides and carbides in aqueous electrolytes. The results were acquired using cyclic voltammetry and a series of electrolyte ion isolation experiments. The ion isolation experiments were performed by substituting the electrolyte ions with counter ions that are known to be inactive. These results provide important insights regarding the charge storage mechanisms for these materials.

2. Experimental

2.1. Material synthesis and characterization

Nanostructured V, Mo and W nitrides and carbides were synthesized via the temperature-programmed-reaction of V₂O₅ (Sigma Aldrich), (NH₄)₆Mo₇O₂₄·4H₂O (81–83% as MoO₃, Alfa Aesar) and WO₃ (Alfa Aesar), respectively. These oxides were reacted with a mixture containing 15% CH₄ and H₂ (Cryogenic Gases) or anhydrous NH₃ gas (Cryogenic Gases) as the temperature was increased linearly to the final soak temperature. Additional details regarding the synthesis conditions can be found elsewhere [18–22]. After synthesis, the materials were quenched to room temperature in the reactant gas then passivated using a flowing mixture of 1% O₂ with He (Cryogenic Gases). Passivation results in the formation of an oxygen-rich protective layer that prevents oxidation of the bulk material when exposed to air.

The materials were characterized using X-ray diffraction with a Cu K α ($\lambda = 0.15404$ nm) source and Ni filter. The crystalline phases were identified using JADE9.0. The physical surface areas were measured by N₂ physisorption using the Brunauer–Emmett–Teller (BET) method with a Micromeritics ASAP 2010 analyzer. Prior to analysis, the materials were degassed in vacuum at 350 °C for 5 h.

The electrochemical stability and capacitance measurements were carried out in aqueous 1 M KOH or 0.5 M H₂SO₄ solutions using cyclic voltammetry. These experiments were performed using a quartz three-electrode cell with an AUTOLAB PGSTAT320N potentiostat. The cell consisted of three compartments, with the working electrode in the center chamber. The working electrode chamber was connected to the reference electrode chamber with a luggin capillary and to the counter electrode chamber with a porous frit. The electrolyte solutions were deaerated with N₂ for at least 20 min before the experiments. A N₂ blanket was maintained in the working electrode chamber during the experiments. A Pt flag was used as the counter electrode. Hg|HgO (0.1 M KOH, Radiometer Analytical) and Hg|HgSO₄ (Sat. K₂SO₄, Radiometer Analytical) were used as reference electrodes in the KOH and H₂SO₄ solutions, respectively.

For the stability assessments, the working electrode consisted of the metal nitride or carbide supported on an Au microelectrode by abrasive adhesion. Each material was cycled at a scan

rate of 50 mV s⁻¹ for 100 cycles within a potential window that was expanded in a step-wise fashion by 0.1 V on both the anodic and cathodic sides until the material showed evidence of instability. The capacitances were measured on macroelectrodes prepared by coating a slurry containing 80% of the active material, 10% graphite (Timcal KS-4) and 10% polyvinylidene fluoride (Kynar) in N-methylpyrrolidinone (Alfa Aesar) solvent onto a Ti foil and then drying the film in vacuum at 80 °C for 8 h. The capacitance was estimated by integrating the area under the cyclic voltammogram (Eq. (1)) [3].

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

Here \hat{C} is the specific capacitance (F g⁻¹), i is the current (A), ΔV is the potential window (V) within which the material was scanned, s is the scan rate (V s⁻¹) and m is the mass of the active material mass (g).

2.2. Ion isolation experiments

In order to determine the electrolyte species participating in the redox reactions, the K⁺, OH⁻, H⁺ and SO₄²⁻ ions were isolated by pairing them with inactive-counter ions. CF₃SO₃⁻ (triflate), (C₂H₅)₄N⁺ (tetraethylammonium) and BF₄⁻ (tetrafluoroborate) were selected as the counter ions as these are known to be redox inactive in the voltage ranges of interest for the nitrides and carbides [3]. The K⁺ and OH⁻ ions were isolated as K(CF₃SO₃) and [(C₂H₅)₄N]OH, whereas the H⁺ and SO₄²⁻ were isolated as HBF₄ and [(C₂H₅)₄N]₂SO₄. Cyclic voltammograms were collected in aqueous solutions containing each of these salts. The solution concentrations were adjusted to achieve constant ionic strengths of 0.1 for K⁺ and 0.3 for SO₄²⁻. The electrolyte solution pH was used to estimate the H⁺ and OH⁻ concentrations and ionic strengths.

3. Results and discussion

Diffraction patterns confirmed that the bulk materials were phase pure (Fig. 1). Physical and electrochemical properties of the materials are listed in Table 1. The surface areas are similar to those reported previously for nanoscale early transition metal nitrides and carbides [19–21].

The VN, VC and β -W₂N electrodes were stable in KOH while the β -W₂C and γ -Mo₂N electrodes were stable in H₂SO₄. The β -Mo₂C material was not stable in either KOH or H₂SO₄ electrolytes. Of the stable nitrides and carbides, VN in KOH (210 F g⁻¹) and γ -Mo₂N in H₂SO₄ (346 F g⁻¹) demonstrated the highest capacitances and widest stability windows. The specific or areal capacitances for all of the nitrides and carbides were significantly higher than those expected for simple double-layer storage (Table 1). These results indicated that pseudocapacitive mechanisms contributed significantly to the overall capacitance.

Given their high capacitances, VN and γ -Mo₂N were selected for more detailed investigation. Cyclic voltammograms for VN and

Table 1
Physical and electrochemical properties of the early transition metal nitrides and carbides.

Material	Surface area (m ² g ⁻¹)	Stability window (V)	Gravimetric capacitance (F g ⁻¹) ^a	Specific capacitance (μ F cm ⁻²) ^b
VN	38	1.1 (KOH)	210	553
VC	6	0.8 (KOH)	2.6	43
β -Mo ₂ C	60	–	–	–
γ -Mo ₂ N	152	0.8 (H ₂ SO ₄)	346	227
β -W ₂ C	16	0.7 (H ₂ SO ₄)	79	494
β -W ₂ N	42	0.8 (KOH)	25	60

^a Gravimetric capacitance estimated using Eq. (1) for scan 25 at scan rate 2 mV s⁻¹.

^b Specific or areal capacitance determined from gravimetric capacitance and physical surface area. Double layer capacitance for most materials is $\sim 25 \mu$ F cm⁻² [3].

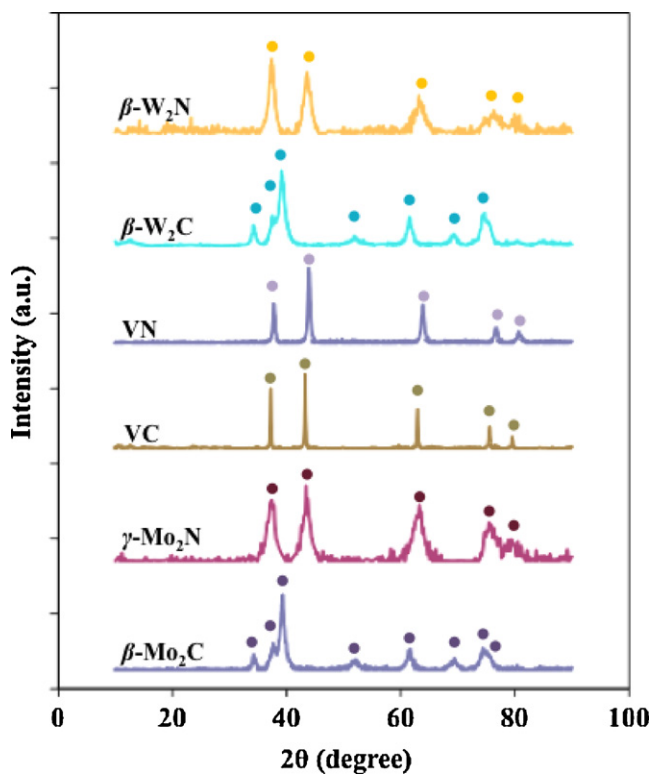


Fig. 1. X-ray diffraction patterns for the early transition metal nitrides and carbides.

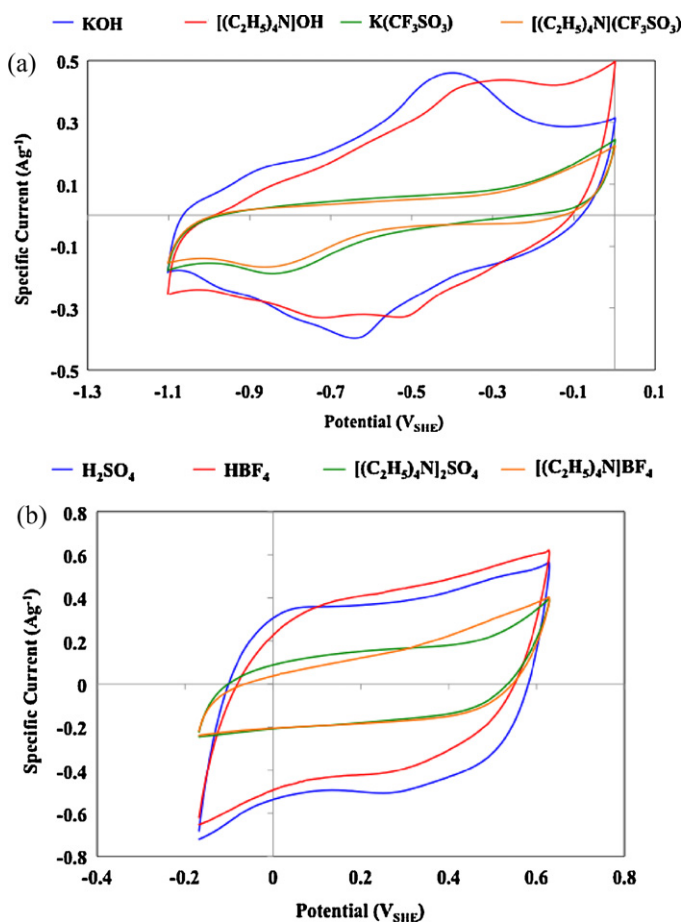


Fig. 2. Cyclic voltammograms for (a) VN and (b) γ -Mo₂N in various electrolytes collected at a scan rate of 2 mV s⁻¹.

Table 2

Capacitances measured for VN from scan 25 in various electrolytes (2 mV s⁻¹).

Electrolyte solution	pH	Capacitance (F g ⁻¹)
KOH (0.1 M)	12.8	234
K(CF ₃ SO ₃) (0.1 M)	9.3	65
[(C ₂ H ₅) ₄ N]OH (0.1 M)	12.9	228
[(C ₂ H ₅) ₄ N](CF ₃ SO ₃) (0.1 M)	8.1	61

Table 3

Capacitances measured for γ -Mo₂N from scan 25 in various electrolytes (2 mV s⁻¹).

Electrolyte solution	pH	Capacitance (F g ⁻¹)
H ₂ SO ₄ (0.1 M)	1.3	380
HBF ₄ (0.1 M)	1.3	340
[(C ₂ H ₅) ₄ N] ₂ SO ₄ (0.1 M)	4.9	140
[(C ₂ H ₅) ₄ N]BF ₄ (0.3 M)	4.2	141

γ -Mo₂N in various electrolytes are illustrated in Fig. 2(a) and (b), and the capacitances are listed in Tables 2 and 3, respectively.

The cyclic voltammograms for VN in 0.1 M KOH clearly showed two redox couples at $-0.42/-0.61$ V and $-0.88/-0.96$ V and a third couple at $-0.77/-0.66$ V. These couples were likely due to successive changes in the oxidation state of vanadium during charge and discharge. The cyclic voltammograms and capacitances for VN in 0.1 M KOH (234 F g⁻¹) and 0.1 M [(C₂H₅)₄N]OH (228 F g⁻¹) were similar suggesting that OH⁻ was a key species in the charge storage mechanism. Cyclic voltammograms and capacitances for VN in 0.1 M K(CF₃SO₃) (65 F g⁻¹) and 0.1 M [(C₂H₅)₄N](CF₃SO₃) (61 F g⁻¹) were similar but significantly lower from those in 0.1 M KOH. Assuming that CF₃SO₃⁻ was inactive, this result suggested that K⁺ played a minor role in the charge storage mechanism and may have been a spectator. Redox peaks for VN in KOH were shifted slightly compared to those in [(C₂H₅)₄N]OH. Given that the current varies as the square-root of the binary diffusion coefficient and electrolyte concentration, it is plausible that the peak shift was a consequence of the differing diffusion coefficients for (C₂H₅)₄N⁺ and K⁺, solution pH values and/or solution conductivities [23]. The peaks observed in the cyclic voltammogram for VN in K(CF₃SO₃) and [(C₂H₅)₄N](CF₃SO₃) at -0.85 V have been attributed to reactions involving minor contaminants in the electrolytes and/or CF₃SO₃⁻.

Cyclic voltammograms for γ -Mo₂N in various electrolytes are illustrated in Fig. 2(b). These cyclic voltammograms did not yield prominent peaks, however, the magnitudes of the capacitances (Table 3) implicated charge storage beyond that expected for formation of the electrochemical double layer. The capacitances for γ -Mo₂N in 0.1 M H₂SO₄ (380 F g⁻¹) and in 0.1 M HBF₄ (340 F g⁻¹) were similar, while those in 0.1 M [(C₂H₅)₄N]₂SO₄ (140 F g⁻¹) and 0.3 M [(C₂H₅)₄N]BF₄ (141 F g⁻¹) were lower. Note that the molarity for [(C₂H₅)₄N]BF₄ was adjusted to produce ionic strength similar to those for the other electrolytes. This result indicated that SO₄²⁻ and BF₄⁻ had similar effects on capacitance and that for γ -Mo₂N in H₂SO₄, the H⁺ was the most important active species for charge storage.

4. Conclusions

Phase pure, nanostructured nitrides and carbides of V, Mo and W were characterized in aqueous KOH and H₂SO₄ electrolytes. VN in KOH and γ -Mo₂N in H₂SO₄ had the highest capacitances. Results from the ion isolation experiments suggested that OH⁻ and H⁺ were the principal species participating in charge storage for VN in KOH and γ -Mo₂N in H₂SO₄, respectively, while K⁺ and SO₄²⁻ were spectators.

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