

Pretreatment Effects on Charge Storage of Early Transition-Metal Carbides and Nitrides

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Introduction

Early transition-metal carbides and nitrides are promising candidates for use in supercapacitor electrodes due to their high electronic conductivities, high surface areas (can exceed 200 m²/g), good electrochemical stabilities and high capacitance [1,2]. For example, the capacitance for VN has been reported to be as high as 1340 Fg⁻¹ in aqueous KOH [3]. This high capacitance has been attributed to pseudocapacitive charge storage involving fast near-surface redox reactions. Recently we observed that pretreatment of the surface to remove the passivation layer significantly improved the capacitances and electrochemical stabilities of early transition-metal carbides and nitrides in aqueous electrolytes. In this paper we present results from characterization including cyclic voltammetry (CV), chronopotentiometry, and electrochemical impedance spectroscopy (EIS), and x-ray photoelectron spectroscopy (XPS) to explain changes in the storage properties caused by pretreatment.

Experimental

The early transition-metal carbides and nitrides of V, W and Mo were synthesized via temperature-programmed-reaction of their oxide precursors with 15% CH₄/H₂ or anhydrous NH₃ followed by passivation in 1% O₂/He at room temperature to form a oxygen-rich passivation layer preventing bulk oxidation on exposure to air [1]. Characterization of the structural properties was performed using nitrogen physisorption (BET surface area) and X-ray diffraction. Prior to the electrochemical characterization, the electrodes were pretreated in 0.3M NaOH aqueous solution for 1 min then rinsed with acetone, ethanol, and ultrapure water [4]. CV was used to establish the stability windows and capacitances for these materials. The capacitance was deconvoluted into double-layer capacitance and pseudocapacitance by means of CV and EIS. Chronopotentiometry was used for further the stability analysis and to determine changes in surface activities caused by pretreatment.

Results and Discussion

The specific capacitance for VN increased by 57% after pretreatment (Figure 1). This enhancement suggests significant improvements in the electrochemical activities. We believe that pretreatment altered the charge storage

mechanism for the carbides and nitrides. We also observed good electrochemical stability after cycling the materials for several thousand cycles. In general, the treated materials were more stable than the passivated materials with higher capacitances.

Figure 2 shows the open circuit potential (OCP) or rest potentials for the passivated and treated VN in acidic medium. The OCP for the treated material was lower than that for the passivated material. We attributed this to differences in surface activities. Using the Nernst equation, we found that the treated VN had a higher pseudocapacitance than the passivated VN. This pseudocapacitive charge-storage mechanism is being investigated using XPS and in-situ x-ray absorption spectroscopy.

The physical and electrochemical properties will be described in terms of a proposed mechanism for pseudocapacitive charge storage.

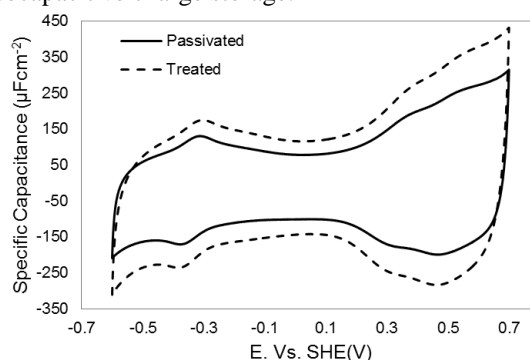


Figure 1: CV of passivated and treated VN in 0.1M H₂SO₄ at 50 mVs⁻¹.

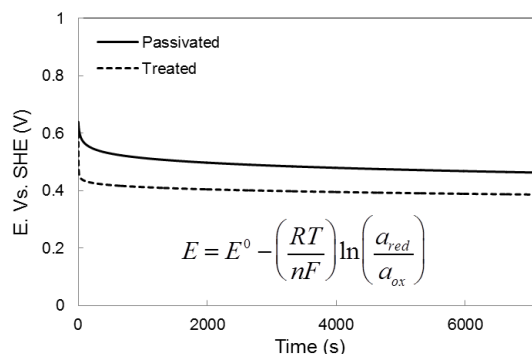


Figure 2: Rest potential of passivated and treated VN in 0.1M H₂SO₄

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