



Effects of surface oxygen on charge storage in high surface area early transition-metal carbides and nitrides



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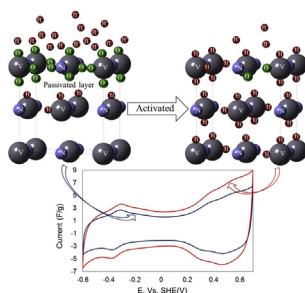
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HIGHLIGHTS

- Activation significantly reduces oxygen content perhaps removing passivation layer.
- Activated (native) materials more electrochemically stable than passivated materials.
- Activation significantly increases surface area, and average pore size.
- Activation significantly increases specific and surface area normalized capacitances.
- Pseudocapacitive charge storage increased.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of surface oxygen on the physical and electrochemical properties of high surface area Mo, V and W carbides and nitrides has been investigated. These materials hold promise for use in supercapacitors and other electrochemical conversion devices. The carbides and nitrides were synthesized using a temperature programmed reaction method and passivated to avoid bulk oxidation on exposure to air. The passivated materials were activated in 0.3 mol dm⁻³ NaOH solution to remove the oxygen-rich passivation layer. This activation resulted in significant changes in the electrochemical stabilities and capacitances. The surface areas for the Mo and W-based materials were higher after activation, with the effect ranging from an 11% increase for Mo₂N to a 208% increase for W₂C. An increase in pore volume and mesopore density was also observed for most of the materials. Interestingly, the VC and W₂C, which were electrochemically unstable in acidic electrolyte in their passivated form, were stable after activation. The capacitances of all of the materials were increased after activation with the effect ranging from 48% for Mo₂N to a 79% increase for (α + β)-Mo₂C. This activation process could be used to improve the performance of carbide and nitride-based supercapacitor electrode materials.

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1. Introduction

Electrochemical capacitors or ‘supercapacitors’ are a relatively new type of energy-storage device that provides high power densities (up to 15 kW kg⁻¹) [1], long cycle life (e.g. >1,000,000) [1] and moderate energy densities (5 Wh kg⁻¹) [2]. They fill the gap

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between conventional high-power capacitors and high-energy batteries. These devices can replace batteries in a number of applications and can complement batteries in hybrid systems by managing high power draws and extending the lifetime [3]. One of the emerging applications for supercapacitors is storage to level the output of intermittent power generation sources such as solar and wind. These devices could facilitate the introduction of renewable electricity into the grid.

Supercapacitors store energy electrostatically at the electrode/electrolyte interface (double-layer capacitance) and/or via fast and reversible surface redox reactions analogous to processes in a battery (pseudocapacitance) [4]. Currently, the high cost and moderate energy density of supercapacitors limits their use. Strategies to increase their energy densities include increasing the capacitance and/or the operating voltage. The material used most often in commercial supercapacitors is activated carbon which is costly and has limited capacitance [2]. Capacitances for these carbons are derived from double-layer formation and typically range up to 125 Fg^{-1} . Energy densities for the corresponding devices can reach 5 Wh kg^{-1} [5,6]. Further enhancements in the performance of these materials will be incremental as increased surface areas are usually derived from micropores that are too

small for the solvated electrolyte ions [4,5]. Over the past few years, significant emphasis has been placed on finding new, low-cost materials that out-perform carbon-based materials for supercapacitor applications.

A number of materials which exhibit pseudocapacitance have been reported including conducting polymers like polyaniline, polypyrrole, polythiophene and their derivatives [7,8] and the oxides of Ru, and Mn [4,9–13]. Hydrated RuO_2 is currently the benchmark pseudocapacitive material with capacitances up to 1300 Fg^{-1} and energy densities in excess of 8 Wh kg^{-1} [4,9], however, the high cost of Ru limits its large-scale use. MnO_2 is a lower cost alternate to RuO_2 , but has a lower electronic conductivity [5] and the capacitances for MnO_2 powders and micrometer-thick films are typically in the range of $150\text{--}220 \text{ Fg}^{-1}$ [14]. Ultra-thin MnO_2 films formed on metal current collectors have been reported to have capacitances near 1000 Fg^{-1} [12,13]. Due to the very low loadings, thin films are best suited for micro-system applications and are not attractive for large-scale industrial applications [12].

Early transition-metal carbides and nitrides have been reported as potential supercapacitor electrode materials [15–18]. Their electrocatalytic properties can be similar to those of noble metals [19]. The carbide and nitride materials can be produced with high

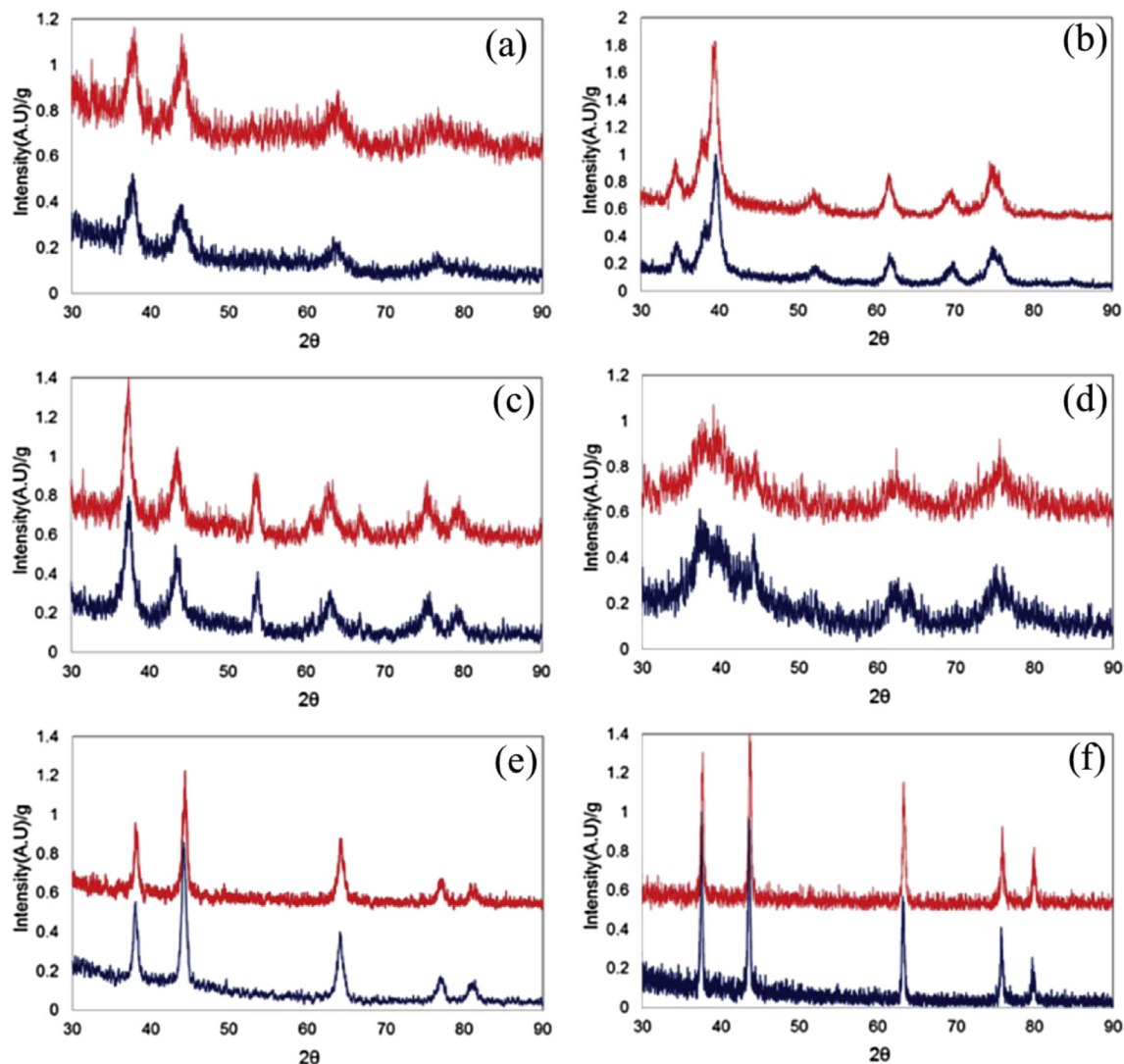


Fig. 1. X-ray diffraction patterns of the passivated (blue) and activated (red) (a) W_2N , (b) W_2C , (c) Mo_2N , (d) $(\alpha + \beta)\text{-Mo}_2\text{C}$, (e) VN and (f) VC . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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