

Anomalous Non-Faradaic Capacitance in Vanadium Nitride Thin Films

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Abstract

Pseudocapacitive or electrochemically active materials can achieve capacitance values up to 10-100 times higher than those obtained by materials working only using an electric double layer (EDL) mechanism. The pseudocapacitive behaviour of several transition metal oxides has been extensively studied in the last decades and assigned to redox (Faradaic) reactions occurring at the surface of the material. Very recently, transition metal nitrides such as Mo_xN , VN or TiN have emerged as promising electrode materials for electrochemical capacitors. These materials are relatively inexpensive and feature a high molar density, good chemical resistance, and, most importantly, in contrast to oxides, they exhibit a very high electronic conductivity value. An impressive gravimetric capacitance of 1300 F g^{-1} (surface capacitance $\sim 3.3 \text{ mF cm}^{-2}$) reported by Choi et al, 2006 [1] for nanosized vanadium nitride has stimulated considerable interest in vanadium nitride as a potential electrode material for energy storing systems – supercapacitors. The postulated mechanism of charge storage in vanadium nitride materials involves redox reactions in the thin surface layer of vanadium oxide while the core vanadium nitride serves exclusively as a conducting platform. In this study we have synthesized pure oxygen-free vanadium nitride films and have found that they are capable of delivering a surface capacitance of up to $\sim 3 \text{ mF cm}^{-2}$ at a potential scan rate of 3 mV s^{-1} and $\sim 2 \text{ mF cm}^{-2}$ at a potential scan rate of 1 V s^{-1} in aqueous electrolytes. Combining electrochemical testing with X-ray photoelectron spectroscopy characterization has revealed that redox reactions play no or little role in the electrochemical response of pure VN, in contrast to the common wisdom stemming from the electrochemical response of oxygen-containing films. An alternative charge storage mechanism (shown in the Figure 1) – space charge accumulation in a subsurface layer of $\sim 100 \text{ nm}$ – was put forward to explain the experimentally observed capacitance of VN films in aqueous electrolytes.

References

[1] D. Choi et al., Adv. Mater., **18** (2006) 1178

Figures

