Vanadium nitride thin films and nanoclusters: combined XPS and electrochemical characterization

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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 behavior of several transition metal oxides has been extensively studied in the last decades and assigned to redox 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. Extremely high specific capacitance values of 1340 F g^{-1} were reported for nanostructured VN [1]. To shed some light on the underlying mechanism of capacitive behaviour of VN we have taken the surface science approach – using thin films and/or supported nanoclusters as model systems and applying surface sensitive techniques (XPS, AFM etc.) in combination with electrochemical testing.

VN films of various thicknesses have been successfully fabricated by direct nitridation of the predeposited pure vanadium film. Stoichiometric and virtually oxygen free VN films were grown on Ta foil in a customized UHV XPS system (XPS) which featured high pressure cell, where V metal film was heated up to 800 ^oC in 1 bar of pure nitrogen gas. VN nanoclusters were grown on HOPG (Figure below). The experimental system also featured an integrated electrochemical cell where sample could be transferred without exposing to air for cyclic voltammetry under Ar atmosphere. We have carried out a combined XPS and electrochemical study of as-prepared and cycled vanadium nitride films in various electrolytes ranging from basic to acidic, and also in industrial organic electrolyte 1.5M $TEA^+BF_4^-$/ACN. A dependence of capacitance on the film thickness was established, showing a saturation of capacitance values once film thickness reaches ~100 nm. At saturation impressive specific capacitance values between 2000 and 3000 µF/cm^2 were achieved in the cyclic voltammetry mode in 1M KOH for scan rates up to 1 V/s. This capacitance two orders of magnitude higher than could be expected from EDL. In the same time cyclic voltammograms and XPS examinations do not reveal redox peaks and vanadium oxidation state variations respectively. Therefore we argue that the pseudocapacitive mechanism evoked in [1] and assigned to redox events involving OH^- species cannot explain detected anomalous surface capacitance of the VN films and its dependence on the film thickness. In contrast we believe that the observed electrochemical properties of the VN films can be related to the space charge formed at the semiconductor-electrolyte interface. On the practical side, high surface-related capacitance values at the high rate shows the promise that VN films hold for microsupercapacitor applications.

References

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

Figures: VN clusters on HOPG: AFM image and cyclic voltammmogram