

Screening of transition metal nitride as possible electrodes for electrochemical capacitors

J.F. Pierson¹, S. Bouhtiyaa¹, R. Lucio Porto², E. Eustache², F. Capon¹, T. Brousse¹¹ Institut Jean Lamour, CNRS, Université de Lorraine, Nancy, France² Institut des Matériaux Jean Rouxel, CNRS, Université de Nantes, Nantes, France

* jean-francois.pierson@univ-lorraine.fr

Although most of the electrodes of electrochemical capacitors (ECs) are either carbon-based or oxides materials, other ceramic materials may also be considered. Choi et al. have shown that vanadium nitride exhibit an impressive capacitance of 1340 F g⁻¹ at a scan rate of 2 mV s⁻¹ in KOH [1]. The authors showed that the composition of the nitride powder and its specific surface area strongly influences the capacitance [2]. Indeed, VN powder with low specific surface area only exhibits a capacitance of 58.3 F g⁻¹ at the same scan rate. Several groups study the electrochemical properties of vanadium nitride [3-5] and but the measured are still ranging in the 100 – 300 F g⁻¹ range. Others nitrides also exhibit interesting capacitance: TiN, Mo₂N, W₂N or RuN [6-8]. However, the literature does not present a systematic screening of the properties of transition metal nitride. Since the electrochemical properties are strongly influenced by geometrical parameters such as the specific surface area, it is necessary to compare nitrides with the same kind of morphology. The reactive sputtering process is a well-known method to synthesize thin films with various stoichiometries and it allows the deposition of coatings with controlled roughness. Thus, the aim of our work is to compare the capacitance of transition metal nitride thin films exhibiting the same specific surface area.

Transition metal nitride (TMN) films were deposited on glass substrates by reactive magnetron sputtering of TM targets. The following transition metals have been studied: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb and Ru. The deposition conditions (current applied to the target and nitrogen flow rate) were adjusted as a function of the reactivity of the transition metal atoms with nitrogen ones. Whatever the transition metal, the morphology of the films is columnar. Co-, Cu- and Ni-based films crystallized in a TM₃N-like structure while the other deposited films exhibit a metal to nitrogen atomic ratio of 1 and. Although the structure of ScN, TiN, VN, CrN, NbN and γ''-FeN is widely described, few information about the structure of MnN and RuN are available in the literature. From X-ray diffraction analyses and Rietveld refinement we show that RuN and MnN crystallise in a ZnS-like structure with lattice constant of 0.451 and 0.428 nm, respectively. Most of the TMN films exhibit a preferred orientation. For the mononitride films the [111] preferred orientation is evidenced by pole figure. Transmission electron microscopy investigations of ruthenium nitride film clearly evidence that the nitride columns are monocristalline (fig. 1). The same kind of behavior has been observed for most of the nitride thin films.

The electrochemical properties of the deposited films were determined by cyclic voltammetry in 1M KOH electrolyte. ScN, Ni₃N, FeN, CrN and NbN have shown a poor capacitance suggesting that only double layer is

involved in the charge storage mechanism. The large capacitance of Co₃N, MnN, RuN and VN and the nearly rectangular shape of the voltammograms suggest a pseudofaradaic process. These nitrides have shown a capacitive behavior at high scan rates due to their high electronic conductivity and fast reversible redox process. The cyclic voltammograms of VN films in 1M KOH evidence a potential window of 1.2 V (from -1.2 to 0 V vs. Hg/HgO). On the other hand, the potential window of RuN thin films is about 0.9 V (from -0.5 to 0.4 V vs. Hg/HgO) (fig. 2). Among the different nitride screened in this study, VN exhibit the highest capacitance.

Finally, VN thin film has been coupled with electrodeposited nickel oxide in order to design an electrochemical capacitor microdevice. VN has been used as negative electrode while NiO was used as the positive one in 1M KOH electrolyte. VN exhibits a pseudo-capacitive behavior while NiO shows a faradaic behavior. This asymmetric microdevice has been operated between 0.5 and up to 1.8 V in aqueous based electrolyte. Long term cycling ability (10,000 charge/discharge cycles) has been demonstrated with interesting energy (1.0 μW h cm⁻²) and power (40 mW cm⁻²) densities

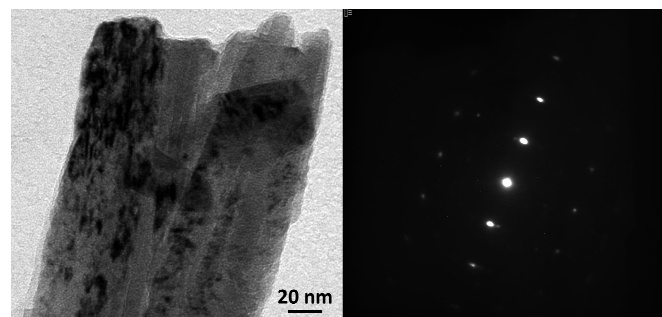


Fig. 1: bright field image of a RuN film and selected area electron diffraction pattern of one column.

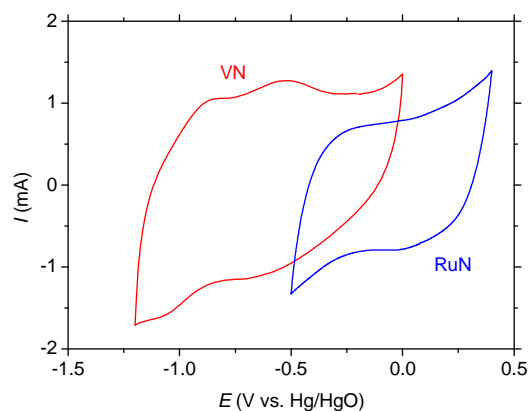


Fig. 2: cyclic voltamogram of VN and RuN thin films at a scan rate of 200 mV s⁻¹ in 1M KOH electrolyte.

References

- [1] Choi et al., Adv. Mater. 18 (2006) 1178
- [2] Choi et al., Electrochem. Solid State Lett. 8 (2005) A418
- [3] Zhang et al., J. Phys. Chem. C 115 (2011) 24381
- [4] Dong et al., Mater. Res. Bull. 46 (2011) 835
- [5] Zhou et al., J. Phys. Chem. Solids 70 (2009) 495
- [6] Pande et al., J. Power Sources 207 (2012) 212
- [7] Choi et al., J. Electrochem. Soc. 153 (2006) A2298
- [8] Bouhtiyaa et al., Scripta Mat. 68 (2013) 659
- [9] Eustache et al. Electrochem. Comm. 28 (2013) 104