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Wettability and Electrochemical studies of macroporous MnO_2 films in hydrophobic and hydrophilic ionic liquids

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Abstract – The present contribution presents the obtention of macroporous MnO_2 films by electrodeposition over polystyrene nanospheres template. A systematic study on how pore size in MnO_2 films affects the wettability by hydrophilic and hydrophobic ionic liquids has been done and the electrochemical performance of this system was evaluated for supercapacitor application.

Supercapacitors based on pseudocapacitance are high power energy devices that involve fast redox reactions. As these reactions occur at the surface of the electrode, the performance of such devices can be improved by using high surface area materials [1]. However, when porous materials are used in order to improve surface area, the wettability by the electrolyte can be compromised which will affect the electrochemical response. The present work presents a systematic study on how pore diameter can affect the wettability by hydrophobic (1-butyl-2,3-dimethyl-imidazolium bis(trifluoromethanesulfonyl)imide - BMMITFSI) and hydrophilic (1-butyl-2,3-dimethyl-imidazolium tetrafluoroborate - $BMMIBF_4$) ionic liquids and the performance of the system as supercapacitor. Ionic liquids present high electrochemical stability, which can improve devices power density and energy when compared with a system based on aqueous electrolyte.

Macroporous MnO_2 electrodes were obtained by galvanostatic electrodeposition from $KMnO_4$ aqueous solution over gold substrate previously covered with polystyrene nanospheres template. The process was monitored by EQCM in order to control the mass of material deposited over spheres of different diameters (100, 300, 460, 600 and 800nm). After electrodeposition, polystyrene template was removed with THF. FESEM images obtained from electrodes have shown that tridimensional macroporous MnO_2 were obtained, with pore diameter of approximately the same diameter of polystyrene nanospheres.

Contact angle measurements were performed by adding 4µL of electrolyte ($LiBF_4$ 0.5mol L^{-1} in $BMMIBF_4$ and LiTFSI 0.5mol L^{-1} in BMMITFSI) over the macroporous film and the angle between solid-air and liquid-air lines was measured. Figure 1 present contact angle in function of pore diameter for both liquids. The results have shown that the wettability varies with pore diameter and is better for hydrophobic ionic liquid. These facts can be explained based on Cassie-Baxter model, in which the air trapped inside the pores cause an increase in contact angle [2]. The resistance caused by the air inside the pores has to be overcome by the capillary force in order to allow liquid entrance into the pores [3].

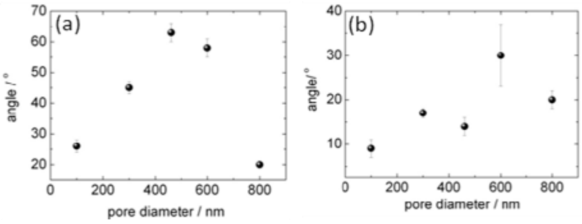

Figure 1: contact angle in function of pore diameter for (a) $LiBF_4$/$BMMIBF_4$ and (b) LiTFSI/BMMITFSI

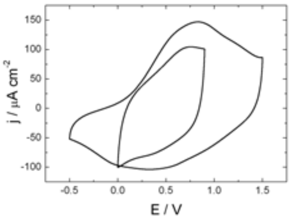

Figure 2: j x E potentiodynamic profile of 0.1µm pore size MnO_2 film. Electrolyte: LiTFSI 0.5mol L-1 in BMMITFSI; scan rate: 0.01V s-1; C.E.: Pt mesh; Ref.: Ag wire

Cyclic voltammetry experiments performed in both electrolytes between 0.0V and 0.9V (vs. Ag/AgCl) have shown that electrochemical response in independent on pore diameter. Higher specific capacitance was obtained with the hydrophobic ionic liquid (figure 2), which is in agreement with the higher wettability achieved with this electrolyte. Experiments performed in a higher voltage (2.0V) have presented an improvement in the electrochemical performance, which turns this ionic liquid a safer, environmentally friend and higher power alternative for supercapacitor application.

References

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