Electronic supplementary information

Effect of the formulation of the electrode on the pore texture and electrochemical performance of manganese dioxide-based electrode for application in hybrid electrochemical capacitor

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Theoretical specific capacitance of MnO_2

The charge involves in a one electron transfer between Mn(III) and Mn (IV) is 1110 C/g and translates into a specific capacitance of 1233 F/g for a 0.9 V potential window. However, if the Mn oxidation states differ from 3+ and 4+ and have not been reached at the negative and positive potential limits, respectively, a higher theoretical specific capacitance could be achieved. The estimated value of 1370 F/g represents the high theoretical value if a variation of about 10% of the oxidation states of manganese species is assumed. The true theoretical value can be determined only if the potential range needed to get a one-electron interconversion between Mn (III) and Mn (IV) is exactly known. For example, a one electron transfer between Mn(III) and Mn (IV) over a 0.8 V potential window with the same theoretical charge of 1110 C/g will translate into a specific capacitance of 1370 F/g. Finally and as mentioned in reference 13 of our manuscript, the theoretical specific capacitance is expected to be at least 1000 F/g, a value not reached with composite electrode.

Morphology of composite electrodes.

SEM micrographs of MnO_2-carbon-PTFE composite electrode obtained at lower magnification clearly show that MnO_2 particles and carbon are homogeneously mixed.

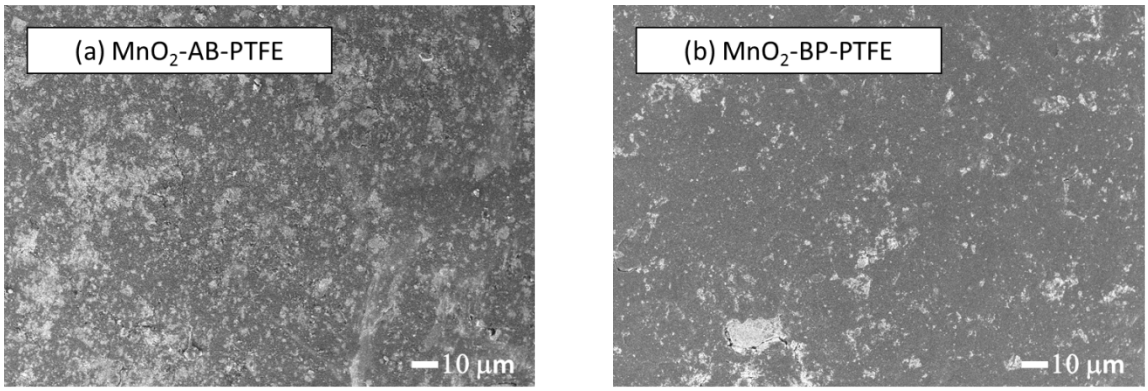

Fig. 1. SEM micrographs of (a) 60 wt. % MnO_2-30 wt. % AB-10 wt. % PTFE, (b) 60 wt. % MnO_2-30 wt. % BP-10 wt. % PTFE.

Calculation of the number of moles of manganese redox sites in MnO_2 and ions in the porous composite electrode.

The following parameters were used for the calculation and an example is given for the 60 wt. % MnO_2-30 wt. % BP-10 wt. % PTFE composite electrode.
Mass of the composite electrode: 5.3 mg
Surface area : 0.25 cm^2
Thickness: 186 µm
M.W. of MnO_2 : 87 g/mol
[K_2SO_4] : 0.65 M
Density of MnO_2 : 5.03 g/cm^3
Density of AB or BP : 1.8 g/cm^3
Density of PTFE: 2.2 g/cm^3
The porous volume of the composite electrode was calculated by subtracting the volume of the active materials (from the mass of the electrode, the proportion of each component and film (thickness x surface area). The number of moles of K^+ ions (2.3 $x10^{-3}$ mmol) is obtained from the porous volume and the concentration of the K_2SO_4 solution. It is clearly smaller (by more than an order of magnitude) than the number of moles of manganese sites (36.6 x 10^{-3} mol).

Coulombic efficiency of MnO_2-carbon-PTFE composite electrodes

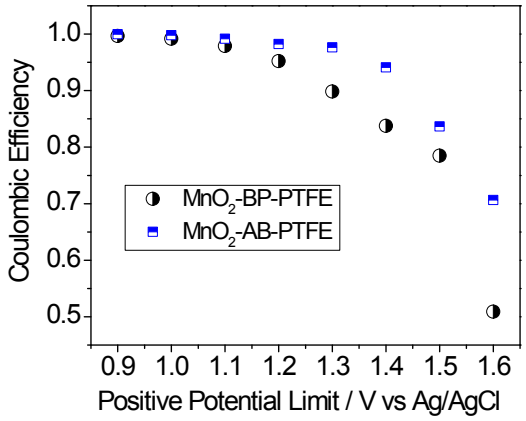

Fig. 2. Variation of Coulombic efficiency of 60 wt. % MnO_2-30 wt. % carbon-10 wt. % PTFE electrodes for different positive potential limit used during the cyclic voltammetry measurements.

Cycling stability of MnO_2-carbon-PTFE composite electrodes

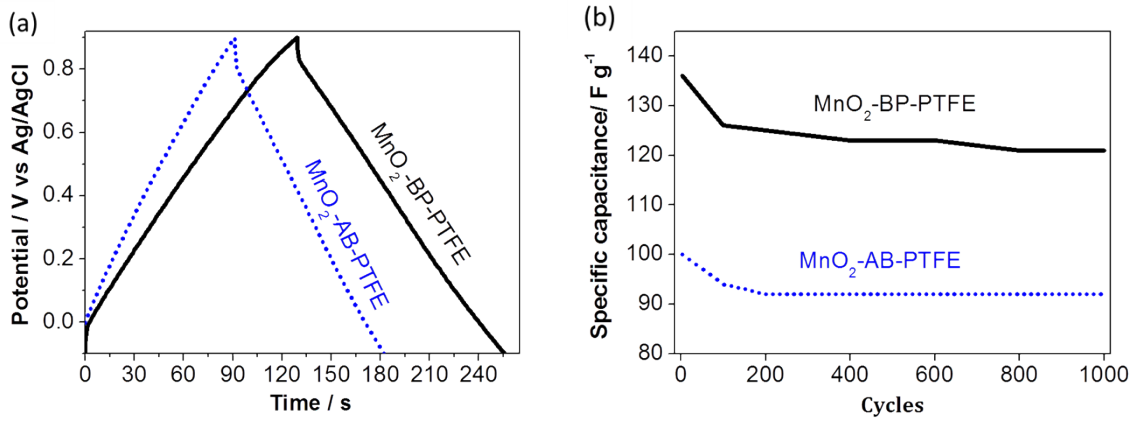

Fig. 3. a) Constant current charge/discharge curves at a current of 1 A g^{-1} of 60 % wt. MnO_2- 30% wt. carbon- 10% wt. PTFE electrodes and b) variation of the specific capacitance of 60 % wt. MnO_2- 30% wt. carbon- 10% wt. PTFE electrodes. The electrolyte for the experiments was a 0.65 M K_2SO_4 aqueous solution.