

Optimisation of an asymmetric manganese oxide/activated carbon capacitor working at 2 V in aqueous medium

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Abstract

The charge storage mechanism of manganese oxide and activated carbon has been studied in aqueous medium in order to optimise an asymmetric (or hybrid) supercapacitor based on these two materials as positive and negative electrode, respectively. Amorphous manganese oxide can be polarised up to potentials of 1.2 V in neutral medium. Under negative polarisation, a pseudocapacitive behaviour of activated carbon has been demonstrated, that is related with reversible hydrogen adsorption in the pores. It allows carbon to be polarised at potential values far from the thermodynamic decomposition of the electrolyte. Balancing the mass of these two materials with pseudocapacitive properties results in a practical cell voltage of 2 V in aqueous medium, with energy densities close to the values obtained with electric double layer capacitors working in organic electrolytes, while avoiding their disadvantages.

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1. Introduction

Energy storage devices can be mainly divided into batteries and capacitors. Rechargeable batteries can store high amounts of energy but with a rather low specific power. On the contrary, electrochemical capacitors can supply higher power than most batteries but the energy density is relatively low [1–2]. The amount of electrical energy (E) accumulated in such capacitors is proportional to the capacitance (C) and voltage (V) according to the formula:

$$E = \frac{1}{2} CV^2 \quad (1)$$

The capacitance depends essentially on the electrode material used, whereas the operating voltage is determined by the stability window of the electrolyte. Aqueous electrolytes

can work in a maximum voltage window of 1 V (the thermodynamic window of water is 1.23 V) with a relatively low equivalent series resistance (ESR). The decomposition voltage of organic electrolytes varies from 3 to 5 V, but the ESR is usually high that precludes to reach easily high powers [2–4]. Such electrolytes are often unstable in presence of activated carbon electrodes and ecologically unfriendly. In addition, supercapacitors based on organic electrolytes are quite expensive because of specific manufacturing conditions, requiring to avoid any contact with air and moisture.

From the foregoing, it results clearly that electrochemical capacitors using aqueous electrolytes would be more attractive from an industrial point of view, but it is necessary to find strategies to increase the amount of energy stored. On the basis of Eq. (1), this purpose can be achieved either by finding materials with high capacitance or by increasing the working potential window.

In this sense, materials where the mechanism for energy storage is based on fast faradic reactions between the electrode and the electrolyte, giving so-called “pseudo-

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capacitance” properties, are showing higher performance than materials presenting pure double-layer capacitance [5]. During the last years, various metal oxides have been proposed for pseudocapacitance purpose [6–10]. Among all the oxides studied, amorphous and hydrated ruthenium oxide (RuO_xH_y) presents the best performance. Here, the pseudocapacitance arises from the overlapping of several redox processes in a reversible way. Capacitance values ca. 760 F g^{-1} have been reported [9–10], but the high cost of RuO_xH_y precludes its use at industrial scale. Therefore, many efforts have been devoted in order to find cheaper materials with similar performance.

Previous studies were predicting a promising behaviour of amorphous manganese oxide, with a specific capacitance of ca. 200 F g^{-1} and a potential window between 0.8 and 1.2 V when using almost neutral electrolytes (KCl, Na_2SO_4 , etc.) [11–17]. However, it is necessary to mention that all these investigations were performed in three-electrode cells, and only the performance of the positive electrode was shown. In a previous work, we were testing the performance of manganese oxide in real two-electrode systems [18]. It was concluded that manganese oxide is not an optimal material for both positive and negative electrodes in symmetric capacitors. The performance of capacitors based on manganese oxide is limited by the two irreversible reactions Mn(IV) to Mn(II) at the negative electrode and Mn(IV) to Mn(VII) at the positive electrode, which potential depends on the electrolyte pH. In particular, applying the conditions usually used in previous studies with three-electrode cells to real capacitors leads to the dissolution of the negative electrode even when the positive electrode can work up to potentials of 1.2 V versus NHE [18].

A very interesting alternative could consist in using manganese oxide as positive electrode and another material as negative electrode in an asymmetric system. Hong et al. [19] were showing for the first time a hybrid system based on MnO_2 as positive electrode and activated carbon as negative electrode, allowing the operating voltage in aqueous medium to be extended up to 2 V. Although the capacitance of manganese oxide is lower than for RuO_2 , the energy densities are comparable due to the high voltage used in the asymmetric system. A recent study [20] explains that a high operating voltage can be reached with this system in aqueous medium because of the combination of the high hydrogen overpotential presented by activated carbon under negative polarisation together with a high oxygen overpotential when MnO_2 is used as positive electrode. However, serious limitations were found when the system was tested at a voltage of 2.2 V, related with H_2 evolution at the negative electrode. The system was optimised for a potential window of 1.5 V with still an interesting electrochemical performance and negligible gas evolution.

The reasons why under negative polarisation activated carbons present a high hydrogen overpotential have never been

documented for hybrid systems, where the positive electrode is from MnO_2 or conducting polymers [19–21]. Therefore, in the present work, we present a deep analysis of the storage mechanism of activated carbon under negative polarisation and manganese oxide under positive polarisation. The understanding of the processes taking place in both electrodes of the asymmetric capacitor during charge and discharge allows us to optimise the system.

2. Experimental

The high purity carbon nanotubes (CNTs) used in this study were prepared by decomposition of acetylene over a powdered $\text{Co}_x\text{Mg}_{1-x}\text{O}$ solid solution catalyst [22]. A composite of amorphous manganese oxide ($\text{a-MnO}_2 \cdot n\text{H}_2\text{O}$) with CNTs was prepared by chemical precipitation of manganese oxide, from KMnO_4 and $\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$ water solutions [11–12] in the presence of carbon nanotubes. The CNTs, as conductivity agent, were added (15 wt% in the final composite) to the KMnO_4 solution before $\text{a-MnO}_2 \cdot n\text{H}_2\text{O}$ precipitation in order to obtain a homogeneous mixture. The mixed solution was stirred during 6 h and the precipitated $\text{a-MnO}_2 \cdot n\text{H}_2\text{O}/\text{CNTs}$ composite was thoroughly washed with deionized water before to be dried at 120°C during 12 h. The characterisation of the material, its electrochemical performance and the profit of using CNTs as additive is detailed elsewhere [18]. The carbon-based electrode was prepared by using the commercial activated carbon PX21 (Maxsorb, Kansai, Japan) with a BET surface area of $2500 \text{ m}^2 \text{ g}^{-1}$.

The capacitor electrodes were films formed by a mixture of the active material ($\text{a-MnO}_2 \cdot n\text{H}_2\text{O}/\text{CNTs}$ composite or activated carbon, 90 wt%) with a binder water suspension (Teflon, 10%). The mixture was thoroughly homogenised in an agate mortar and dried at room temperature before being rolled into a thin film of uniform thickness. Electrode pellets were cut with a surface of 1 cm^2 , which corresponds approximately to a mass of 10 mg. Two electrode capacitors were built with a glassy fibrous separator and gold current collectors, using a Teflon Swagelok® type system. Different aqueous electrolytic solutions have been used: 2 mol L^{-1} KNO_3 with a pH of 6.4 or with a modified pH by the addition of KOH or HNO_3 . The values of capacitance were estimated by voltammetry (scan rate of potential from 2 to 10 mV s^{-1}) and galvanostatic charge/discharge cycling (VMP-Biologic-France). Experiments were also done in Teflon three-electrode cells by using Pt and $\text{Hg}/\text{Hg}_2\text{SO}_4$ as auxiliary and reference electrodes, respectively. All potentials are reported versus normal hydrogen electrode (NHE).

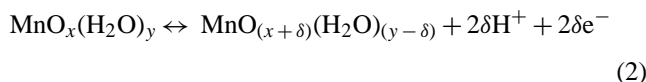
Impedance spectroscopy measurements were performed on the symmetric and asymmetric capacitors at the rest potential of each cell (VMP-Biologic-France). An ac amplitude of 20 mV was applied to reach the steady-state cell voltage. Data were collected in the range of 10,000–0.001 Hz.

3. Results and discussion

3.1. Charge storage mechanism for manganese oxide and activated carbon electrodes

3.1.1. Manganese oxide composite

Hydrous oxides as amorphous manganese oxide have a pseudocapacitive behaviour, attributed to reversible redox transitions involving protons and/or cations exchange with the electrolyte [15]. For example, in neutral medium the reaction should follow the equation:



where $\text{MnO}_x(\text{H}_2\text{O})_y$ and $\text{MnO}_{(x+\delta)}(\text{H}_2\text{O})_{(y-\delta)}$ indicate interfacial manganese oxide at high and low oxidation states, respectively. Fig. 1 shows the cyclic voltammogram (CV) obtained on the manganese oxide composite with a three-electrode cell in aqueous 2 mol L^{-1} KNO_3 medium with a pH of 6.4 or with a pH of 10 (obtained by adding KOH to the previous medium). As it was reported in a previous work [18], the total potential range in which manganese oxide can be polarised depends on the electrolyte pH. The reason is that the maximum and minimum values of polarisation potential are controlled by the reactions Mn(IV) to Mn(VII) and Mn(IV) to Mn(II), respectively, which are irreversible because of the solubility of both, Mn(VII) and Mn(II) in water. Since the reaction potentials depend on pH, we can see in Fig. 1 that in a basic pH medium ca. 10, manganese oxide can be reversibly polarised in the potential range from 0.05 V (potential of the reaction Mn(IV) to Mn(II) [23]) to 0.98 V (potential of the reaction Mn(IV) to Mn(VII) [23]), while in a neutral pH medium ca. 6.4 the reversible polarisation range is from 0.47 V (potential of the reaction Mn(IV) to Mn(II) [23]) to 1.19 V (potential of the reaction Mn(IV) to Mn(VII) [23]). These facts limit the use of manganese oxide

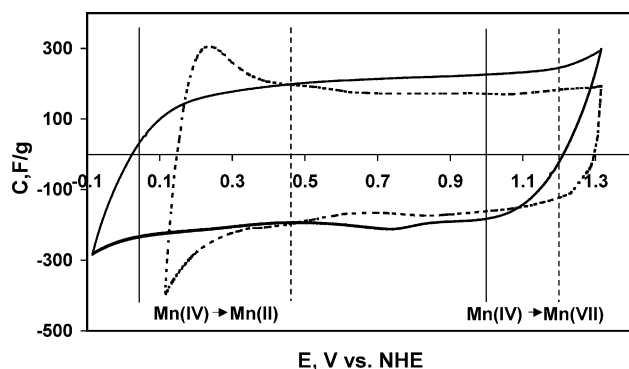


Fig. 1. Cyclic voltammetry in a three-electrode cell using the manganese oxide/CNTs composite as working electrode, Pt as auxiliary electrode and Hg/Hg₂SO₄ as reference electrode. Scan rate of potential 2 mV s^{-1} . The results are presented vs. NHE at two different values of pH: (a) 6.4 (dashed line) and (b) 10 (full line). The vertical lines (dashed for pH 6.4; full for pH 10) superimposed on the curves represent the potential of both irreversible transitions Mn(IV) to Mn(II) and Mn(IV) to Mn(VII).

as positive and negative electrode in a symmetric capacitor. By contrast, the high values which can be achieved under positive polarisation, i.e. 1.2 V in a medium of pH 6.4, makes this material very attractive for the positive electrode in a hybrid system [19–20].

The positive polarisation of manganese oxide could be also limited by O₂ evolution because of water decomposition from the electrolyte. However, a high oxygen overpotential was found independently of the electrolyte pH. As an example, the thermodynamical oxygen evolution should start at a potential of 0.85 V for pH 6.4 and 0.64 V for pH 10. In fact, Fig. 1 shows that in both pH media, the manganese oxide composite can be polarised up to higher potential values without showing the fast current leap of a gas evolution in the CV. This profitable result is purely related with a shift of pH down to lower values, because H⁺ species are generated on the manganese oxide electrode under positive polarisation according to reaction (2).

3.1.2. Activated carbon

The activated carbon charge storage mechanism has been mainly assessed to double layer capacitance. High performance supercapacitors can be developed by enhancing the electrode–electrolyte interface by the use of high surface area activated carbons [24].

Fig. 2 shows the CV in a three-electrode cell for the PX21 carbon electrode in neutral pH medium ca. 6.4 (2 mol L^{-1} KNO_3) at different values of negative polarisation cut-off. The quite rectangular shape of the CV down to a potential cut-off of -0.4 and -0.8 V, with comparable values of positive and negative current, proves a pure capacitive and reversible behaviour in these potential ranges. However, at pH 6.4, the H₂ thermodynamic evolution should theoretically start at -0.38 V. This phenomenon, which should be expressed by a fast current leap, is not observed down to potentials of -0.8 V, indicating a high H₂ overpotential. This behaviour could be explained by a local pH increase on the surface of the electrode due to the water decomposition producing OH⁻ anions confined in the micropores according to

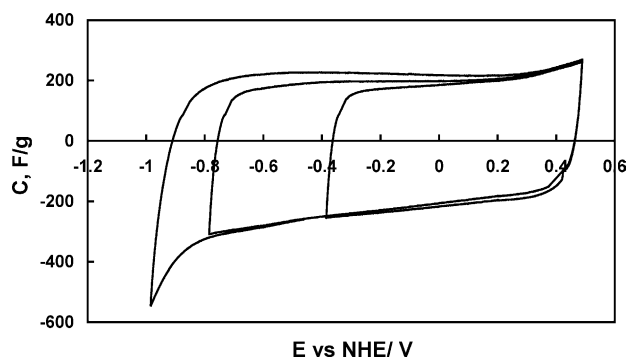


Fig. 2. Cyclic voltammetry in a three-electrode cell using the activated carbon PX21 as working electrode, Pt as auxiliary electrode and Hg/Hg₂SO₄ as reference electrode in 2 mol L^{-1} KNO_3 electrolyte. Scan rate of potential 2 mV s^{-1} . The results are presented vs. NHE.

the reaction:



where (H) stands for nascent hydrogen. The H_2 overpotential found for the activated carbon, ca. 0.5 V, is lower than for non-porous glassy carbon electrodes in the same electrolytic conditions, ca. 0.9 V [25–26]. However, considering that the overpotential is a function of the current density, these values cannot be directly compared because of the very different surface area of both types of materials.

Additionally, a careful analysis of Fig. 2 indicates that when the potential cut-off reaches a value of -0.8 V, which is lower than the equilibrium potential for hydrogen evolution, ca. -0.38 V, the anodic current slightly increases in comparison with the CV performed at a potential cut-off of -0.4 V. In fact, as it was shown previously [27], during the carbon electrode polarisation to potentials lower than the one of water decomposition, the nascent hydrogen produced according to reaction (3) is immediately adsorbed in the micropores of the activated carbon. Later, during the anodic sweep, the adsorbed hydrogen is reversibly electrooxidised and by this reason an increase of the anodic current is observed. This effect is more visible in Fig. 2 if the potential cut-off is decreased to a value of -1 V. Close to this potential there is a fast current increase, which demonstrates a faster kinetics of hydrogen production, and correlatively the anodic current is higher. Hence, the lower the value of negative polarisation, the higher the amount of hydrogen produced and adsorbed in carbon, and the higher the anodic current due to the reversible hydrogen electrooxidation.

To summarise, down to potentials cut-off higher than the thermodynamic value for hydrogen evolution, the storage mechanism of the activated carbon is simply by charging the electrical double-layer in the electrode–electrolyte interface. When the potential cut-off is decreased down to more negative values, there is a pseudocapacitive contribution due to a reversible hydrogen adsorption in the activated carbon, which extent is controlled by the value of the negative cut-off potential. This results in an increase of the total specific capacitance of the electrode, from 170 F g^{-1} at a potential cut-off of -0.4 V to 230 F g^{-1} when the potential cut-off is decreased down to -1 V. Hence, the pseudocapacitive behaviour related with the reversible hydrogen adsorption is the reason for the good performance of activated carbon as negative electrode in different asymmetric systems [19–21].

3.2. Optimisation of the asymmetric manganese oxide/activated carbon system

From the above results, it is possible to affirm that a hybrid capacitor can be developed by the combination of two materials with pseudocapacitive behaviour. The manganese oxide composite is very attractive for the positive electrode because it can be polarised up to values higher than the electrochemical O_2 evolution. In addition, the activated carbon shows

an unique behaviour under negative polarisation with a very high hydrogen overpotential.

Taking into account that the overpotentials for O_2 and H_2 evolution strongly depend on the electrolyte pH, the two electrodes were tested with electrolytes of different pH in order to obtain the maximum working voltage window in full charge of the asymmetric system. The electrolytic solution was based on $2 \text{ mol L}^{-1} \text{ KNO}_3$ with a pH 6.4 and the pH was increased or decreased by adding potassium hydroxide or nitric acid, respectively. The two electrodes, i.e. the manganese oxide composite or the activated carbon, were tested separately in a three-electrode cell using Pt wire and $\text{Hg}/\text{H}_2\text{SO}_4$ as auxiliary and reference electrode, respectively. Cyclic voltammetry experiments were performed in order to know the potential limits of both materials in each electrolyte of different pH.

Fig. 3 shows a $E(\text{V})$ –pH diagram where the lines for the thermodynamic equilibrium potentials of O_2 (line 1) and H_2 (line 2) evolution from water decomposition are included. In addition, lines 3 and 4 represent the pH dependence of the thermodynamic reversible potentials for the Mn^{4+} oxidation to Mn^{7+} and Mn^{4+} reduction to Mn^{2+} , respectively.

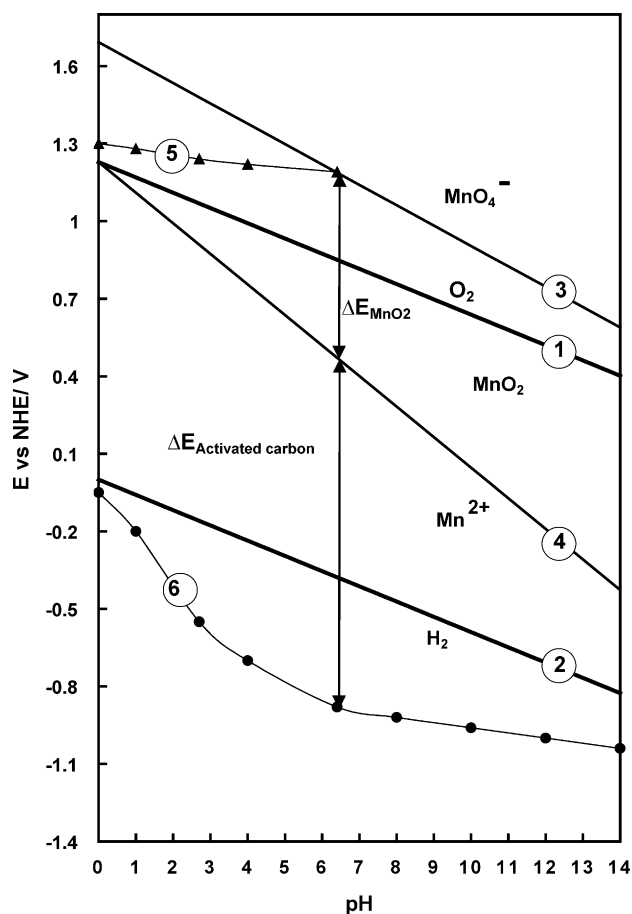


Fig. 3. Potential–pH diagram. Lines 5 and 6 represents the kinetical limits for O_2 evolution on a- MnO_2 and for H_2 evolution on activated carbon, respectively.

As it was pointed out before, the maximum potential up to which manganese oxide can be polarised will be given either by the oxygen evolution from the electrolyte decomposition or by the non-reversible oxidation of Mn^{4+} to Mn^{7+} . In both cases, if one of these processes takes place, a fast current leap will be observed in the CV and the limit of the positive or negative polarisation will be determined by the potential at the beginning of this current leap. Line 5 in Fig. 3 represents the experimental values of the limit potential for the positive polarisation obtained at different values of pH. It can be observed that the O_2 overpotential on manganese oxide increases when increasing the electrolyte pH. However, at pH higher than 6.4, the maximum limit for the positive polarisation will be controlled by the irreversible reaction Mn^{4+} to Mn^{7+} . The lowest value of potential to which manganese oxide can be polarised is controlled by the irreversible redox reaction Mn^{4+} to Mn^{2+} (line 4) in the total pH range.

Line 6 in Fig. 3 contains the experimental values of H_2 evolution potentials when testing the activated carbon in electrolytes of different pH. CV experiments allowed the H_2 overpotential values to be determined from the beginning of the current leap characteristic of gas evolution on the electrode surface. The overpotential, represented by the difference between lines 2 and 6, is small at low or high pH and it reaches a maximum in neutral pH electrolytes.

Hence, from Fig. 3, it results clearly that for building a full capacitor working with the maximum potential window using manganese oxide as positive electrode, an electrolyte of acidic pH is not adequate. The potential window in which manganese oxide can be cycled is very small, as extracted from the difference between lines 3 + 5 and line 4 in Fig. 3. An electrolyte with alkaline nature can provide a wider potential window for cycling a manganese oxide electrode. Taking into account that the stability window of the electrolyte is limited by the curves 3 + 5 and 6, for cycling a full capacitor with manganese oxide as positive electrode and activated carbon as negative electrode, a pH close to 6.4 seems to be optimal. At pH 6.4, manganese oxide will be stable between 0.47 V (limited by the Mn^{4+} to Mn^{2+} reaction) and 1.19 V (limited by the Mn^{4+} to Mn^{7+} reaction). At the same pH, activated carbon can be used down to negative potentials of -0.88 V (limited by H_2 evolution) and from potentials of 0.47 V, which is the inferior stability value for manganese oxide. Therefore, if the total cell voltage is expressed as the sum of the potential range for manganese oxide and for activated carbon, it is possible to conclude that for an asymmetric capacitor it could be extended up to 2.1 V in an aqueous medium of pH 6.4.

For illustrating this result, Fig. 4 shows the CVs obtained in a three-electrode cell for the manganese oxide composite and the activated carbon in the 2 mol L^{-1} KNO_3 electrolyte with pH 6.4, using a Pt wire as auxiliary electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ as reference electrode. The specific capacitance obtained in these conditions is 160 F g^{-1} for manganese oxide and 180 F g^{-1} for the activated carbon electrode. In Fig. 4, it can be observed that the two materials are stable in a different range of potentials. Hence, in order to obtain a capacitor

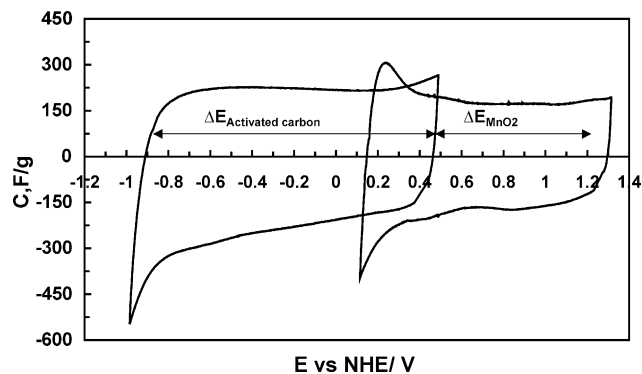


Fig. 4. Comparative cyclic voltammograms in a three-electrode cell using manganese oxide or activated carbon as working electrode, Pt as auxiliary electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ as reference electrode in 2 mol L^{-1} KNO_3 electrolyte. Scan rate of potential 2 mV s^{-1} .

operating in a 2.1 V voltage window, it is necessary to control the experimental conditions for the manganese oxide to work in the potential range from 0.47 to 1.19 V and the activated carbon electrode in the range from 0.47 to -0.88 V.

At this point, it should be mentioned that in a symmetric capacitor, with two electrodes from the same material and having the same mass, the applied voltage splits equally between the two electrodes. However, if the two electrodes are different in nature as in an asymmetric system, the voltage will split depending on the capacitance of each electrode. The capacitance of each electrode is related with the mass and the specific capacitance of the active material. In order to get the optimum cell voltage in an asymmetric capacitor, a mass balance between the two electrodes will be necessary.

For this purpose, it must be considered that the charges at positive (q_+) and negative (q_-) electrodes should be balanced and should also equal to the amount of ions consumed from the electrolyte (q_i). The maximum charge which can be stored will be determined by the smallest value among q_+ , q_- and q_i , as it was described by Zheng [28]. In the present study, since an excess of concentrated electrolyte is used, the maximum energy density of the cell will be limited by the positive or the negative electrode and the charge balance will follow the relationship $q_+ = q_-$. The charge stored by each electrode depends on the specific capacitance (C), the potential range for the charge/discharge process (ΔE) and the mass of the electrode (m) following Eq. (3):

$$q = C * \Delta E * m \quad (4)$$

and in order to get $q_+ = q_-$, the mass balancing will be:

$$\frac{m_+}{m_-} = \frac{C_- * \Delta E_-}{C_+ * \Delta E_+} \quad (5)$$

On the basis of the specific capacitance values and potential ranges found at pH 6.4 for the manganese oxide composite and activated carbon, the optimal mass ratio between the electrodes should be $m_{\text{MnO}_2}/m_{\text{carbon}} = 2.1$. Fig. 5 shows the cyclic voltammograms at different cell voltages for an asymmetric two electrode cell a- MnO_2 /activated carbon prepared

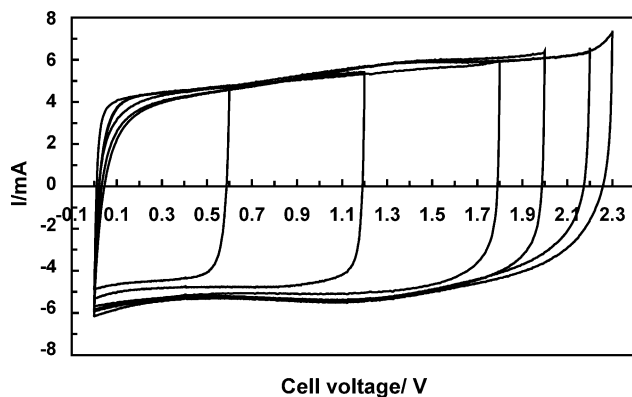


Fig. 5. Cyclic voltammograms on an optimised asymmetric manganese oxide/activated carbon capacitor in $2 \text{ mol L}^{-1} \text{ KNO}_3$ electrolyte. Scan rate 10 mV s^{-1} ; $m_{\text{MnO}_2} = 4.6 \text{ mg}$, $m_{\text{Activated carbon electrode}} = 9.7 \text{ mg}$.

with the optimal electrolyte and mass ratio between the electrodes. The capacitor shows an ideal capacitive behaviour with a rectangular CV curve at voltage windows up to 2.2 V.

Fig. 6 shows the galvanostatic charge–discharge curves of the same asymmetric capacitor for different maximum cell voltages. The figure demonstrates that the specific discharge capacitance of the cell increases with voltage, and up to a value of 2 V the behaviour is capacitive with symmetric charge–discharge lines. However, when the maximum cell voltage is set to 2.2 V, a non-capacitive behaviour with non-symmetric charge–discharge lines is found. Therefore, in order to find the optimal cell voltage, the coulombic efficiency (η) was calculated as:

$$\eta = \frac{q_d}{q_c} \quad (6)$$

where q_d and q_c are the total amount of discharge and charge of the capacitor obtained from the galvanostatic experiments presented in Fig. 6. Fig. 7 represents the coulombic efficiency and the average specific discharge capacitance (C_s) of both electrodes versus the cell voltage. C_s was calculated accord-

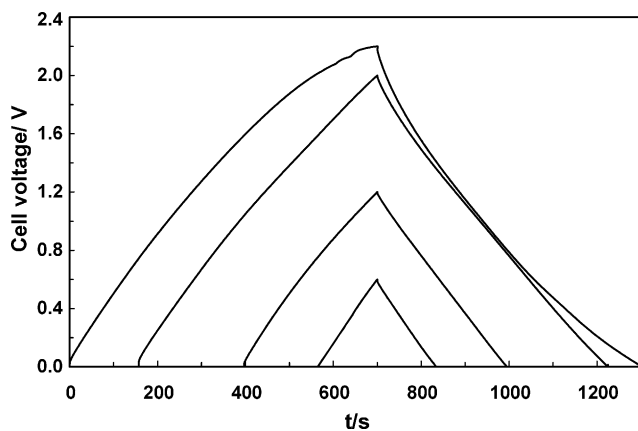


Fig. 6. Galvanostatic charge–discharge curves ($I = 100 \text{ mA g}^{-1}$) of the asymmetric manganese oxide/activated carbon capacitor in $2 \text{ mol L}^{-1} \text{ KNO}_3$ electrolyte.

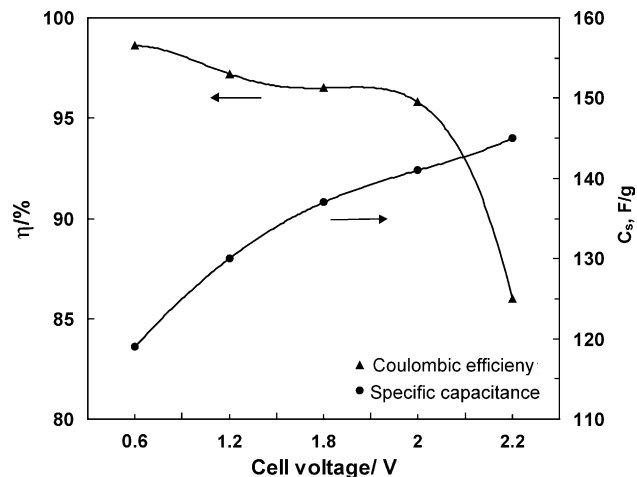


Fig. 7. Coulombic efficiency and specific capacitance C_s of the asymmetric manganese oxide/activated carbon capacitor in $2 \text{ mol L}^{-1} \text{ KNO}_3$ electrolyte vs. the cell voltage.

ing to Eq. (6) [21,29]:

$$C_s = \frac{4C}{M} \quad (7)$$

where C is the total capacitance of the cell and M is the total mass of the two electrodes. Whereas the capacitance increases with the cell voltage, the coulombic efficiency decreases drastically when the voltage is higher than 2 V. This behaviour is probably related with the fact that hydrogen produced during the negative polarisation of the activated carbon electrode is not completely adsorbed in carbon, forming di-hydrogen which evolves [27]. Therefore, the cell voltage should not be higher than 2 V.

Fig. 8 shows the specific discharge capacitance of the asymmetric capacitor charged at 2 V as a function of the number of galvanostatic charge/discharge cycles. The specific discharge capacitance decrease of about 12% during the first 40 cycles is related with the equilibration of both electrode potentials. Once the system is stabilised, Fig. 8 confirms that upon charging at 2 V the discharge capacitance reaches

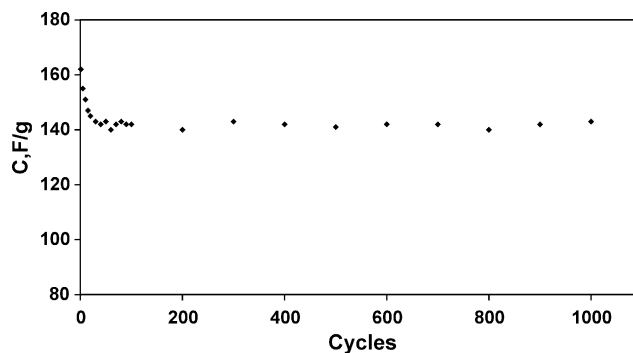


Fig. 8. Specific discharge capacitance (per total mass of both electrodes) of the asymmetric manganese oxide/activated carbon capacitor in $2 \text{ mol L}^{-1} \text{ KNO}_3$ electrolyte vs. the number of cycles. Operating voltage: 2 V.

Table 1

Comparative performance obtained from impedance spectroscopy and cyclic voltammetry experiments on the symmetric manganese oxide/manganese oxide and activated carbon/activated carbon capacitors and on the asymmetric manganese oxide/activated carbon capacitor

Electrode material (+/–)	ESR at 10 Hz (Ω)	t_d (s)	V_{\max} (V)	C_s ($F\ g^{-1}$)	E ($Wh\ kg^{-1}$)	P_{\max} ($kW\ kg^{-1}$)
Activated carbon/activated carbon	0.44	0.34	0.7	180	3.6	51
Manganese oxide/manganese oxide	1.56	0.81	0.6	160	1.9	3.8
Manganese oxide/activated carbon	0.54	0.26	2	140	21.0	123

a value, which keeps constant during the next 1000 cycles. Hence, the good cycle life of the capacitor during this relatively high number of cycles indicates that the experimental conditions, such as the electrolyte, the electrodes mass ratio and the cell voltage, are optimised allowing the system to work reversibly at 2 V in aqueous medium. Anyway, further experiments testing the cycle life with a higher number of cycles should be performed in order to assure a practical utilisation of this device.

3.3. Performance comparison between asymmetric and symmetric systems

Symmetric and asymmetric two-electrode systems were prepared in $2\ mol\ L^{-1}$ KNO_3 electrolyte by using: (i) activated carbon as positive and negative electrode, (ii) the manganese oxide/CNTs composite as positive and negative electrode and (iii) the manganese oxide/CNTs composite as positive electrode and activated carbon as negative electrode. Fig. 9 presents the Nyquist plots for the three kinds of capacitors. The equivalent series resistance (ESR) can be extracted from the high frequency (10 kHz) part of the curves. As it could be expected, the ESR of the symmetric manganese oxide capacitor is higher than the ESR obtained for the sym-

metric activated carbon capacitor, due to the differences in conductivity of the two-electrode materials. However, when an asymmetric system is built by combining the two materials, the ESR is close to the value for activated carbon one. Fig. 9 also shows that at low frequency, the imaginary part of the impedance curves approaches, in all cases, to a vertical line indicating a capacitive behaviour.

Table 1 summarises the data obtained from the impedance spectroscopy experiments presented in Fig. 9, such as the resistance (ESR) and the time constant (t_d), together with the data given by cyclic voltammetry performed on the same cells, such as the maximum cell voltage (V_{\max}) and the specific capacitance (C_s). In addition, the specific energy (E) was calculated by using Eq. (1) and the maximum specific power (P_{\max}) was calculated according to Eq. (7):

$$P_{\max} = \frac{V_{\max}^2}{4ESR \times M} \quad (8)$$

where M is the total mass of both electrodes (including binder and conductivity agent). After analysing all the data contained in Table 1, it is possible to conclude that the performance of the hybrid capacitor is much better than for any of the symmetric systems. In particular, the specific energy, which can be extracted from the asymmetric manganese oxide/activated carbon capacitor is 5–10 times higher than for a symmetric system working in the same aqueous medium.

4. Conclusion

In the present work, the charge storage mechanism of manganese oxide and activated carbon have been studied in order to optimise an asymmetric system using manganese oxide and activated carbon as positive and negative electrode, respectively.

Manganese oxide presents a pseudocapacitive behaviour due to fast faradaic reactions in the electrode/electrolyte interface. Under positive polarisation, potential values higher than the thermodynamic O_2 evolution potential can be reached, being limited by the irreversible $Mn(IV)$ to $Mn(VII)$ reaction.

Activated carbons are usually used for symmetric electrochemical double layer capacitors due to the availability of materials with a high specific surface area. We have demonstrated unique pseudocapacitance properties of activated carbons under negative polarisation in aqueous medium. The voltammetric analysis showed that high overpotential values

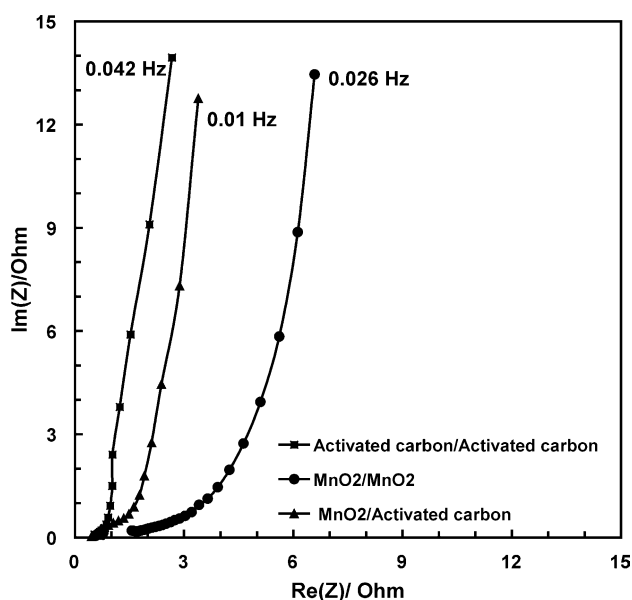


Fig. 9. Nyquist plots of the symmetric manganese oxide/manganese oxide and activated carbon/activated carbon capacitors and of the asymmetric manganese oxide/activated carbon capacitor. Electrolyte $2\ mol\ L^{-1}$ KNO_3 in water.

for H₂ evolution could be reached, that allows to significantly increase the potential window. Hydrogen produced by water decomposition at potentials lower than the thermodynamic value is immediately adsorbed in the carbon porosity, being reversibly electrooxidized during the anodic scan. In this case, the pseudocapacitive properties of activated carbon are related with the redox mechanism of hydrogen in the pores.

Taking profit of the observations performed on both materials, an asymmetric capacitor could be optimized in aqueous medium by combining manganese oxide and activated carbon, as positive and negative electrodes, respectively. The optimized system, where the charge storage mechanism of both electrodes is of pseudocapacitive type, gives a practical cell voltage of 2 V in aqueous medium, with energy densities close to the values obtained with electric double layer capacitors working in organic electrolytes. Due to the various advantages of aqueous over organic electrolytic medium, it is worth to deeply investigate the electrochemical characteristics of systems based on this concept.

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References

- [1] B.E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic, Plenum Publishers, New York, 1999.
- [2] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [3] P.L. Taberna, P. Simon, J.F. Fauvarque, *J. Electrochem. Soc.* 150 (2003) A292.
- [4] D. Qu, H. Shi, *J. Power Sources* 74 (1998) 99.
- [5] B.E. Conway, V. Rirss, J. Wojtowicz, *J. Power Sources* 66 (1997) 1.
- [6] N.L. Wu, *Mater. Chem. Phys.* 75 (2002) 6.
- [7] T.C. Liu, W.G. Pell, B.E. Conway, *Electrochim. Acta* 44 (1999) 2829.
- [8] E.E. Kalu, T.T. Nwoga, V. Srinivasan, J.W. Weidner, *J. Power Sources* 92 (2001) 163.
- [9] J.P. Zheng, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) L6.
- [10] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.
- [11] H.Y. Lee, J.B. Goodenough, *J. Solid State Chem.* 144 (1999) 220.
- [12] H.Y. Lee, S.W. Kim, H.Y. Lee, *Electrochem. Solid State Lett.* 4 (2001) A19.
- [13] S.C. Pang, M.A. Anderson, T.W. Chapman, *J. Electrochem. Soc.* 147 (2000) 444.
- [14] J. Jiang, A. Kucernak, *Electrochim. Acta* 47 (2002) 2381.
- [15] C.C. Hu, T.W. Tsou, *Electrochim. Acta* 47 (2002) 3523.
- [16] Y.U. Jeong, A. Manthiram, *J. Electrochem. Soc.* 149 (2002) A1419.
- [17] C.C. Hu, T.W. Tsou, *Electrochem. Commun.* 4 (2002) 105.
- [18] E. Raymundo-Piñero, V. Khomenko, E. Frackowiak, F. Béguin, *J. Electrochem. Soc.* 152 (2005) A229.
- [19] M.S. Hong, S.H. Lee, S.W. Kim, *Electrochem. Solid State Lett.* 5 (2002) A227.
- [20] T. Brousse, M. Toupin, D. Bélanger, *J. Electrochem. Soc.* 151 (2004) A614.
- [21] J.H. Park, O.O. Park, *J. Power Sources* 111 (2002) 185.
- [22] S. Delpeux, K. Szostak, E. Frackowiak, S. Bonnamy, F. Béguin, *J. Nanosci. Nanotech.* 2 (2002) 481.
- [23] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solution*, National Association of Corrosion Engineers, Houston, TX, 1996.
- [24] E. Frackowiak, F. Béguin, *Carbon* 39 (2001) 937.
- [25] J. Wang, U.A. Kirgoz, J.W. Mo, J. Lu, A.N. Kawde, A. Muck, *Electrochem. Commun.* 3 (2001) 203.
- [26] H.P. Dai, K.K. Shiu, *J. Electroanal. Chem.* 419 (1996) 7.
- [27] K. Jurewicz, E. Frackowiak, F. Béguin, *Appl. Phys. A* 78 (2004) 981.
- [28] J.P. Zheng, *J. Electrochem. Soc.* 150 (2003) A484.
- [29] F. Fusalba, R. Gouerec, D. Villers, D. Belanger, *J. Electrochem. Soc.* 148 (2001) A1.