Nanostructured manganese dioxides: Synthesis and properties as supercapacitor electrode materials

E. Beaudrouet, A. Le Gal La Salle*, D. Guyomard

Univ. Nantes, Institut des Matériaux Jean Rouxel, UMR 6502, B.P. 32229, 44322 Nantes Cedex 3, France

1. Introduction

Electrochemical capacitors are charge-storage devices exhibiting high power density, with good reversibility and cycleability, which can be used in various electric systems. Research in this area has been focused on the development of different electrode materials such as various forms of carbon, conducting polymers and transition metal oxides. Carbon-based materials present the highest surface areas, and function essentially as double-layer capacitors (separation of charge at the interface between a solid electrode and an electrolyte), with specific capacitances reaching 320 F g\(^{-1}\) in aqueous electrolytes [1–7]. Various transition metal oxides presenting charge-storage mechanism based on pseudocapacitance arising from fast and reversible faradic reaction [8–10] involving motion of ions and electrons into the material itself are also good candidates for capacitors. Among them, RuO\(_2\).H\(_2\)O is the most promising, with a specific capacitance exceeding 1300 F g\(^{-1}\) and a good cycleability [11–18]. Nevertheless, this material is toxic and expensive, so that other oxides are needed.

Due to their natural abundance coupled with their environmental compatibility, manganese oxides are commonly used in batteries, and in the case of capacitor electrodes, it seems that MnO\(_2\) shows better performances than other oxides such as Mn(OH)\(_2\), Mn\(_2\)O\(_3\) and MnO\(_2\), with a pseudocapacitive behaviour associated to a theoretical capacitance in the range 1100–1300 F g\(^{-1}\) [19–24]. Experimentally, the capacitance can exceed 600 F g\(^{-1}\), i.e. close to that is obtained with RuO\(_2\), but only for very thin layers (1 \(\mu\)g cm\(^{-2}\)) of dense materials [20,25–31]. And in this case, a strong dependence on the thickness of the deposit was observed. For instance a study performed on a nanostructured MnO\(_2\) prepared with chitosan showed that the capacitance decreases from 400 F g\(^{-1}\) to 177 F g\(^{-1}\) when the deposited mass increases from 50 \(\mu\)g cm\(^{-2}\) to 200 \(\mu\)g cm\(^{-2}\) [32]. For birnessite-like compounds prepared by electro oxidation of acid aqueous solutions of MnSO\(_4\) onto stainless-steel collectors, the capacitances vary in the 70–150 F g\(^{-1}\) range depending strongly on the thickness of the layer [33]. When the oxidation of MnSO\(_4\) is performed in Na\(_2\)SO\(_4\)/CH\(_3\)COONa mixtures, the capacitance decreases from 220 F g\(^{-1}\) to 50 F g\(^{-1}\) as the deposited mass increases from 100 \(\mu\)g cm\(^{-2}\) to 4 mg cm\(^{-2}\) [34]. Of course, correlations were observed between morphologies that are obtained using different synthesis routes and specific capacitances [29,35,31]. Synthesis routes leading to amorphous compounds with high surface areas were extensively studied and capacities of 265–320 F g\(^{-1}\) and of 210–240 F g\(^{-1}\) were obtained in the case of an electrodeposited compound directly used as a capacitor electrode of 130–150 \(\mu\)g cm\(^{-2}\) [20] or 150–180 \(\mu\)g cm\(^{-2}\) [36], respectively. Values reaching 270 F g\(^{-1}\) were reported for thin layers (50 \(\mu\)g cm\(^{-2}\)) of birnessite xerogels prepared by reduction of NaMnO\(_4\) by fumaric acid [37].

© 2008 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +33 2 40 37 39 13; fax: +33 2 40 37 39 95. E-mail address: Annie.Legal@cnrs-imn.fr (A. Le Gal La Salle).
are less numerous. Using mild hydrothermal oxidative treatment of Mn$^{2+}$ salts, it is possible to obtain poorly crystallized birnessite compounds. When surfactant molecules are added during the synthesis, capacities reaching 310 F g$^{-1}$ are observed for electrodeposits of 0.4–0.5 mg cm$^{-2}$ directly used as capacitor electrode [11]. Interesting results are also obtained with coatings (0.25 mg cm$^{-2}$) of MnOOH and Mn$_3$O$_4$ single crystal mixtures [17,38].

All studies cited above concern thin deposits that have been tested as capacitor electrode directly after synthesis. In other cases, manganese dioxides are first prepared and then mixed with carbon black and a binder in order to achieve the composition of a porous composite deposit of some mg cm$^{-2}$ (powder-based electrodes of porous materials). When amorphous manganese dioxides are used, the specific capacitances rarely exceed 200 F g$^{-1}$ [11,25,39–45], even if a synthesis realized by reduction of potassium permanganate in chloroform leads to MnO$_2$ compounds with a capacitance of 260 F g$^{-1}$ at very slow cycling rate [46]. A similar method is used for the preparation of substituted Mn$_{1-y}$Al$_y$O$_2$$^{1-}$ (with A = Co, Al) was also reported, emphasizing the importance of the surface area as well as the morphology, and especially of the pore size distribution [51].

Composite electrodes including thin films of nanostructured MnO$_2$ were also prepared using various methods. A manganese dioxide nanowire electrode into an aluminium oxide template was prepared into a sol–gel solution of Mn(CH$_3$COO)$_2$ and citric acid; it presents a capacitance of 165 F g$^{-1}$ [52]. Manganese oxide/multiwalled carbon nanotubes composites have been successfully synthesized [53] and used as electrode material in supercapacitors [54].

Fig. 1. Flow chart describing the various materials being synthesized and the sequence used. For each material, the structure (2D for MnO$_2$ rancieite-type phase and α for α-MnO$_2$), the type of morphology (LB for large blades, SB for small blades, 0 when blades are not seen, S when sticks can be seen, S$^+$ when the sticks are more numerous and S$^+$ when the sticks cover completely the blades), the BET surface area and the capacitance obtained at the 2nd cycle at 2 mV s$^{-1}$ are given. “n.d.” stands for “not determined”.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structural type</th>
<th>(x)</th>
<th>Mn(^{III})/Mn(^{IV}) ratio</th>
<th>(n)</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>(C_{2mV/s}^{-1}) (F g(^{-1}))</th>
<th>(C_{5mV/s}^{-1}) (F g(^{-1}))</th>
<th>(C_{10mV/s}^{-1}) (F g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>K20</td>
<td>2D-MnO(_2)</td>
<td>0.34</td>
<td>0.93</td>
<td>n.d.</td>
<td>23</td>
<td>28</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>K20H</td>
<td>2D-MnO(_2)+α-MnO(_2)</td>
<td>0.07</td>
<td>0.94</td>
<td>0.50</td>
<td>52</td>
<td>52</td>
<td>28</td>
<td>19</td>
</tr>
<tr>
<td>Na20</td>
<td>2D-MnO(_2)</td>
<td>0.36</td>
<td>0.72</td>
<td>n.d.</td>
<td>11</td>
<td>n.d.</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>Na20H</td>
<td>2D-MnO(_2)</td>
<td>0.03</td>
<td>0.70</td>
<td>0.80</td>
<td>120</td>
<td>n.d.</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>K60</td>
<td>2D-MnO(_2)</td>
<td>0.37</td>
<td>0.94</td>
<td>n.d.</td>
<td>n.d.</td>
<td>75</td>
<td>43</td>
<td>22</td>
</tr>
<tr>
<td>K60H</td>
<td>2D-MnO(_2)+α-MnO(_2)</td>
<td>0.07</td>
<td>0.94</td>
<td>0.77</td>
<td>93</td>
<td>112</td>
<td>82</td>
<td>45</td>
</tr>
<tr>
<td>K60(H)(^2)</td>
<td>α-MnO(_2)</td>
<td>&lt;d.l.</td>
<td>0.94</td>
<td>1.45</td>
<td>150</td>
<td>105</td>
<td>79</td>
<td>46</td>
</tr>
<tr>
<td>K60(H)KH</td>
<td>α-MnO(_2)</td>
<td>&lt;d.l.</td>
<td>0.93</td>
<td>1.64</td>
<td>206</td>
<td>95</td>
<td>72</td>
<td>39</td>
</tr>
<tr>
<td>Na60</td>
<td>2D-MnO(_2)</td>
<td>0.35</td>
<td>0.70</td>
<td>n.d.</td>
<td>11</td>
<td>38</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>Na60H</td>
<td>2D-MnO(_2)</td>
<td>0.03</td>
<td>n.d.</td>
<td>n.d.</td>
<td>45</td>
<td>22</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Na60(H)(^2)</td>
<td>2D-MnO(_2)</td>
<td>&lt;d.l.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>95</td>
<td>17</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>K100</td>
<td>2D-MnO(_2)</td>
<td>0.37</td>
<td>n.d.</td>
<td>n.d.</td>
<td>25</td>
<td>n.d.</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>K100H</td>
<td>2D-MnO(_2)+α-MnO(_2)</td>
<td>0.03</td>
<td>0.93</td>
<td>n.d.</td>
<td>59</td>
<td>49</td>
<td>28</td>
<td>18</td>
</tr>
<tr>
<td>Na100</td>
<td>2D-MnO(_2)</td>
<td>0.37</td>
<td>0.80</td>
<td>n.d.</td>
<td>16</td>
<td>91</td>
<td>42</td>
<td>23</td>
</tr>
<tr>
<td>Na100H</td>
<td>2D-MnO(_2)</td>
<td>0.03</td>
<td>0.68</td>
<td>n.d.</td>
<td>129</td>
<td>80</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>Na100(H)(^2)</td>
<td>2D-MnO(_2)</td>
<td>&lt;d.l.</td>
<td>0.75</td>
<td>n.d.</td>
<td>136</td>
<td>100</td>
<td>75</td>
<td>40</td>
</tr>
</tbody>
</table>

Values noted <d.l. are smaller than the detection limit of the EDX analysis. n.d. stands for “not determined”.

slightly different chemical compositions, morphologies, and surface areas, was obtained. The use of these MnO\(_2\) materials as electrodes in capacitors was then investigated, and correlations between the physical and chemical properties of the compounds and the observed capacitance values were made.

2. Experimental

2.1. Synthesis of the materials

Rancieite-type layered manganese oxides for lithium batteries have been prepared by Leroux et al. \([59]\) using a method derived from that already proposed by Tsuji et al. \([61]\). In order to obtain rancieite-type layered manganese oxides containing K\(^+\) or Na\(^+\) cations, 100 ml of 2 mol l\(^{-1}\) HCl was added to 300 ml of 1 mol l\(^{-1}\) KMnO\(_4\) or NaMnO\(_4\) and the mixture was kept at temperatures of 20°C, 60°C or 100°C for 10 h. The products were then washed repeatedly with distilled water, until almost free from the resulting KCl or NaCl. Thereafter, products are noted K(or Na)\(\_T\), where \(T\) is the ion-exchange temperature. These syntheses are summarized in Fig. 1.

In order to achieve the elimination of alkali-ion, and also in the aim of increasing their BET surface area, some samples, after the first proton-exchange reaction, were submitted to a second treatment in 1 M HNO\(_3\) (two stirring steps) followed by a rinsing step in distilled water. The corresponding samples being noted K(or Na)\(\_T\)(H)\(^2\) (see Fig. 1).

In an attempt to try to increase the BET surface area of the K60H sample, a subsequent alkali-ion exchange was made by mixing this sample with a large excess of equimolar solutions of 1 mol l\(^{-1}\) KCl and 1 mol l\(^{-1}\) KOH for 5 days. The product was washed with distilled water and noted K60HK. A subsequent proton exchange (two successive stirrings in 1.5 l of 1 M HNO\(_3\) followed by a final proton exchange step in distilled water) leads to the K60HKH sample. The list of prepared samples appears in Table 1 and Fig. 1.

2.2. Characterization of the samples

The title compounds were characterized by a combination of techniques including X-ray diffraction (XRD), energy dispersive X-ray (EDX) analysis, BET surface area measurements, thermal analyses and X-ray photoelectron spectroscopy.

XRD patterns were recorded at RT on a Siemens D5000 diffractometer using Cu K\(α\) radiation, from 10\(^°\) to 75\(^°\) (2\(θ\)), with steps twice in 1.5 l of 1 M HNO\(_3\), and finally washed with distilled water (thereafter this complete preparation process will be called proton-exchange reaction). Fig. 1 depicts the sequence used for the preparation of these compounds.

In order to achieve the elimination of alkali-ion, and also in the aim of increasing their BET surface area, some samples, after the first proton-exchange reaction, were submitted to a second treatment in 1 M HNO\(_3\) (two stirring steps) followed by a rinsing step in distilled water. The corresponding samples being noted K(or Na)\(\_T\)(H)\(^2\) (see Fig. 1).

In an attempt to try to increase the BET surface area of the K60H sample, a subsequent alkali-ion exchange was made by mixing this sample with a large excess of equimolar solutions of 1 mol l\(^{-1}\) KCl and 1 mol l\(^{-1}\) KOH for 5 days. The product was washed with distilled water and noted K60HK. A subsequent proton exchange (two successive stirrings in 1.5 l of 1 M HNO\(_3\) followed by a final proton exchange step in distilled water) leads to the K60HKH sample. The list of prepared samples appears in Table 1 and Fig. 1.

![Fig. 2. XRD powder patterns of samples K60 (a), K60H (b) and K60HKH (c).](image)

![Fig. 3. TG curve (1 K min\(^{-1}\)) of K60H in air.](image)
of 0.3° (2θ) and a step time of 1 s. JEOL 5800 V and 6400 V scanning electron microscopes (SEM) were used for EDX analysis and morphology examination, respectively. BET measurements were done with nitrogen adsorption after outgasing the samples at 100 °C under vacuum for 15 h. Thermal analyses were made on a Setaram TGS-2 TGA system in air at a rate of 1 K min⁻¹. A Leybold LHS12 ESCA unit was used to record the XPS spectra (XPS mode).

2.3. Preparation of the electrodes and electrochemical testing

Composite electrodes were prepared by mixing the active material with graphite (Alfa Aesar, conducting grade, −200 mesh), acetylene black (Alfa Aesar, >99.9%, surface area 80 m² g⁻¹) and poly(tetrafluoroethylene) (PTFE) dried powder in the following weight ratios: 70/12/12/6. The mixtures were cold rolled into 100 µm thick films. Small pieces of film (surface of 0.7 cm × 1 cm and mass in the 20–30 mg range) were then pressed at 500 MPa onto a stainless-steel grid. The connection between the grid and the copper wire linked to the potentiostat was protected from the electrolyte with epoxy resin.

Electrochemical tests were made in potentiodynamic mode using a VMP Biologic system at 2 mV s⁻¹ during the first 10 cycles, 5 mV s⁻¹ during the 10 following cycles, and finally at 10 mV s⁻¹. A three-electrode cell was used, in which the working electrode is the electroactive compound containing grid, the reference electrode a Ag⁺/Ag electrode and the counter electrode a large platinum sheet. All measured voltages are given versus the Ag⁺/Ag reference electrode. The voltage was varied between −0.05 V and 0.85 V. The electrolyte was a 0.1 mol l⁻¹ K₂SO₄. The specific capacitance C (F g⁻¹) of a given composite electrode was determined by integrating the cyclic voltammogram to obtain the voltammetric charge (Q), and subsequently dividing this charge by the mass of the composite electrode (m) and the width of the voltage window (ΔE = 0.9 V), i.e. \( C = Q / (\Delta E \times m) \). The specific capacitance of the active material was calculated by dividing the specific capacitance of the composite electrode by the weight percentage of active material in this electrode, after subtraction of the influence of acetylene black (specific capacitance of 12 F g⁻¹ [25]).

3. Results and discussion

3.1. Characterization of the synthesized samples

The XRD patterns of some samples are presented in Fig. 2. Not-exchanged products are not well crystallized, as shown in Fig. 2a for sample K60, which gives only four broad peaks situated roughly at 2θ = 12°, 24°, 37° and 66°. For these samples, the diagrams are very similar to those obtained by Leroux et al. [59] for rancieite-type phases of general formula K(or Na)ₓMnOᵧ·nH₂O, with an interlayer distance of roughly 7.4 Å. This phase is thereafter noted “2D-MnO₂”. Diagrams of all K(or Na)ₓ samples are similar to that of 2a, with no significant difference in the interlayer spacing, independent of the alkali cation or the temperature synthesis. The formation of rancieite-type phases in acidic medium is in accordance with previous results [59,61]. The diagram of proton-exchanged samples K20H, K60H and K100H presents the superimposition of the peaks of the 2D-phase and of new peaks, suggesting the formation of a new phase existing simultaneously with the 2D-MnO₂.
phase, as shown for sample K60H in Fig. 2b. The interlayer distance decreases, reaching now 7.2 Å. Subsequent proton- or alkali-ion exchange steps induces a crystallization improvement of the new phase, leading to diagrams similar to that of sample K60HKH presented on Fig. 2c, in which the two broad peaks observed at 2θ = 24° and 37° for not-exchanged samples have disappeared. With peaks at 13°, 18°, 29°, 38° (instead of 37°), 42°, 50°, 57° and 61°, Fig. 2c is characteristic of the α-MnO₂ phase [71]. Diagram 1b is therefore characteristic of a mixture of 2D-MnO₂ and α-MnO₂. This transformation of K-containing rancieite-type compounds into α-MnO₂ is in agreement with literature: among syntheses of α-MnO₂, some are two-step processes, with, as the intermediate product, a layered MnO₂ structure [72–74]. On the contrary, for proton-exchanged samples Na20H, Na60H, Na60(H)₂, Na100H and Na100(H)₂ the XRD diagrams remain similar to that of 2a, with no α-MnO₂ formation. These results should be compared to those of previous experiments, as for instance those made by Lin et al. [75] for electrochemically prepared α-MnO₂. In this latter study, manganese dioxide were prepared from different M₂SO₄ (where M = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ or Mg²⁺) solutions, and only K⁺- or Rb⁺-containing solutions allowed the synthesis of the α phase. Authors explained this result by the inappropriate size of the other cations that cannot stabilise the 2 × 2 tunnel structure of α-MnO₂ [76]. The results of X-ray diffraction studies are collected in the first column of Table 1 and in Fig. 1. It evidences clearly that in all cases the reduction of MnO₄⁻ in acidic medium leads to rancieite-type compounds, and that it is only in the case of K-containing compounds that the cation/proton exchange leads to the formation of α-MnO₂.

The different K(or Na)/Mn ratios were determined by EDX analysis, and the corresponding x values are given in Table 1. Before proton exchange, the alkali content lies between 0.34 and 0.37, regardless of the alkali cation, in accordance with results already published for similar compounds [59,64,77]. After a first proton exchange in acidic medium, the alkali content becomes very weak, and slightly larger for potassium-containing samples. After two successive proton exchange (samples K60(H)² and Na100(H)²), the alkali content becomes smaller than the detection limit of the EDX analysis. When K60H is submitted to a potassium-exchange reaction (sample K60HK), the potassium content comes back, just slightly less than that of the not-exchanged compound K60, and after a subsequent proton exchange operation (sample K60HKH), the potassium content is again comparable to the value obtained for the K60H sample, thus confirming the perfect reversibility of the K⁺/H⁺ ion-exchange reaction already established by Kanoh et al. [77].

X-ray photoemission spectra of MnO₂-type compounds present characteristic peaks near 642 eV, 654 eV, 529 eV and 85 eV, corresponding respectively to the Mn 2p₃/₂, Mn 2p₁/₂, O 1s and Mn 3s energetic levels. As it was the case for rancieite-type manganese oxides [59], the Mn 2p spectrum does not show satellite peaks at 5 eV to higher energies than the main peaks observed near 642 eV and 654 eV. It shows that no Mn²⁺ is present in the material [35,78,79], as it is the case for compounds revealed by our EDX results. It has been demonstrated that the measurement of the width of the system of two merged peaks observed at 85 eV (Mn 3s energetic level) allows the determination of the average
manganese oxidation state [42,80,81]. A calibration curve was first made with reference compounds and mixtures of them; then values of Mn$^{IV}$ percentage, defined as the ratio $r = \frac{\text{Mn}^{IV}}{\text{Mn}^{III} + \text{Mn}^{IV}}$, were determined and are given in Table 1. Potassium-containing compounds, and compounds derived from them by exchange reactions, exhibit the same $r$ value: 0.93–0.94. For sodium-containing samples and compounds derived from them by ion-exchange, the $r$ values are smaller, perhaps due to the greater electronegativity (Pauling classification) which allows a deeper reduction of manganese, and more dispersed, lying between 0.68 and 0.80. Such values agree with results already reported for birnessite prepared by reduction of aqueous permanganate solutions [59,70].

Characteristic thermal behaviour in air of different samples was studied in order to improve their characterization and to precise their water content. Indeed, it is known [13,26,49] that cation diffusion in hydrated electrodes occurs via hopping of alkaline ions and H$^+$ ions between $\text{H}_2\text{O}$ and $\text{OH}^-$ sites. Therefore a larger content of adsorbed water is expected to enhance the cation diffusion in the electrode, and therefore can lead to an increase in the observed pseudocapacitance. An example is given in Fig. 3 for K60H. As observed in the case of rancieite-type manganese oxides [59] or for $\text{MnO}_2$ amigbels [62], the weight loss process is rather fast up to 100 °C, becomes much slower at higher temperature, and speeds up again around 500 °C. Nevertheless there is no clearly defined plateau before 700 °C. For alkali-free samples, the final product obtained at this temperature was unambiguously identified as $\text{Mn}_2\text{O}_3$ from its XRD pattern. For these samples, the $r$ values given in Table 1 were inferred from TG experiments. The water content of the samples are different and, as expected, samples obtained after successive exchange procedures, as K60(H)$^2$ and K60HKH, are more hydrated.

For alkali-containing samples, the shape of the TG curves is similar. Nevertheless, as already observed by Leroux et al. [59], the final products of thermal decomposition are mixtures of $\text{Mn}_2\text{O}_3$ and Na$_{\alpha}\text{MnO}_2$ for Na-containing samples and mixtures of Mn$_3\text{O}_4$ and Ke$\text{MnO}_4$ with 0.45 ≤ $\alpha$ ≤ 0.55 for potassium-containing samples.

In order to complete materials characterization, the surface areas were also determined and results are given in Table 1 and recalled in Fig. 1. The successive exchange procedures induce an increase in the BET surface areas, which are smaller than 30 m$^2$ g$^{-1}$ for NaT and KT, comprised between 40 and 130 m$^2$ g$^{-1}$ for NaTH and KTH and respectively equal to 136, 150 and 206 m$^2$ g$^{-1}$ for Na100(H)$^2$, K60(H)$^2$ and K60HKH samples. This result is in accordance with the high surface area of 300 m$^2$ g$^{-1}$ which has been reported for a compound obtained by an initial reduction of $\text{KMnO}_4$ or NaMnO$_2$ by maleic acid and followed by a complex set of proton-exchange steps [82].

### 3.2. Morphological study of the samples

The morphology of the compounds was studied by scanning electron microscopy. Samples K20 and K60 are very similar, with agglomerates of 5–10 μm made of spheres with ≥1 μm in diameter. Each sphere exhibits an open texture looking like "sand rose" with large blades. Samples presenting this type of structure are therefore noted “LB” in Fig. 1. This texture is associated to surface areas in the range of 20–25 m$^2$ g$^{-1}$ (cf. Table 1). As an example, Fig. 4a and b presents scanning electron micrographs of sample K60.

Sodium-containing samples are very similar, with about the same size of particles and particles agglomerates (Fig. 4c), but with less numerous blades explaining the lower surface area compared to K-based samples.

It seems also that there is also an influence of the synthesis temperature on the microstructure: although the samples prepared at 20 °C and 60 °C are very similar, it seems that the boiling of the mixture has eroded the blades, leading in the case of Na100 to a morphology presenting smaller blades, and therefore called “SB” in Fig. 1, and in the case of K100 to the total disappearance of blades, and therefore called “0” in Fig. 1. The comparison of samples Na20, Na100 and K100 is presented in Fig. 5.

Potassium-containing samples obtained after a proton exchange procedure remain organized in agglomerates. Instead of being composed of blades of homogeneous shape, the open texture of the spheres is made of mixtures of particles with previous shape (blades of sand roses), and with a new shape (sticks of 500 nm × 40–50 nm), generating an increase of the surface areas. An example is shown in Fig. 6 for sample K60H. The appearance of sticks seems to be associated to the presence of smaller blades, and this type of morphology is mentioned as “SB-S” (for coexistence of small blades and sticks) in Fig. 1. This suggests that, in our case, differences of morphology before and after proton exchange are due to a reorganization correlated to the presence of the $\alpha$-$\text{MnO}_2$ phase in this compound. This observation is in accordance with the morphology described by Subramanian et al. [47] for spherical agglomerates $\alpha$-$\text{MnO}_2$ nanorods prepared under hydrothermal conditions. In the case of sample K60HKH (Fig. 7) the reorganization of particles into agglomerates of sticks is more important (we noted the corresponding morphology SB-S$^+$ in Fig. 1), and correlated to an increase of the surface area, reaching 206 m$^2$ g$^{-1}$. The morphology of K60(H)$^2$ (noted SB-S$^-$ in Fig. 1) is intermediary between those of K60H and K60HKH, as it is the case of its surface area.

For sodium-containing samples Na20H, Na60H and Na60(H)$^2$, the proton exchange procedure leads to larger agglomerates (10–15 μm) of spherical sand roses (0.5–1 μm diameter) with an
important development of the open texture into more numerous large blades, in accordance with the increase of surface areas, but without sticks (and therefore with no change in the blades size). An example is shown in Fig. 8 for Na60H. This confirms that, in agreement with XRD results, the \( \alpha \)-MnO\(_2\) phase is not obtained in this case.

For samples Na100H and Na100(H)\(^2\), the amount and size of blades can be comparable to that obtained for Na100. All these samples have a “SB”-type morphology (see Fig. 1).

Fig. 8. SEM micrographs of sample Na60H.

3.3. Electrochemical characterization of the samples and discussion

Fig. 9, obtained for sample K60HKH during the 2nd cycle at 2 mV s\(^{-1}\), illustrates the typical electrochemical behaviour of all samples. It is different from the classical rectangular curve observed in the case of pure capacitive phenomena, and is characteristic of a pseudocapacitative charge-storage mechanism arising from a fast, reversible faradic reaction, as expected for this type of compound [1,8–10,25,42,45,51,55]. The curve also reveals the presence of a large internal resistance, visible although the scan rate is only 2 mV s\(^{-1}\). The experimental capacitance of the active K60HKH material, extracted from this curve after subtraction of the influence of acetylene black, is 95 F g\(^{-1}\). This value is comparable to what is obtained for similar samples synthesized by permanganate reduction and used as power-based electrodes of similar mass per electrode surface (\textit{vide supra}) [25,40,42,44,45].

Capacitances measured at 2 mV s\(^{-1}\), at the second cycle, for the different samples, are given in Table 1. The “K60” and “Na100” families present the best results, with capacitances ranging from 75 F g\(^{-1}\) to 112 F g\(^{-1}\). Contrary to what was observed in some cases [33], there is no direct influence of the oxidation state of manganese, because similar high capacitances are obtained for Na100(H)\(^2\) and K60(H)\(^2\) (with similar surface areas) in spite of their disparity in the oxidation state of manganese. Similarly, K20 and Na60 present comparable low capacitances (28 F g\(^{-1}\) and 38 F g\(^{-1}\), respectively) but different Mn\(^{IV}\)/Mn\(^{II}\) ratios of 0.93 and 0.70, respectively.

It is also not obvious to interpret the influence of the water content: the sample K60HKH, although it is more hydrated than K60H, presents a smaller capacitance, contrary to results described in refs. [13,26,49].

Fig. 10 illustrates the influence of the surface area on the capacitance. An increase of the BET surface area, as observed when transforming sample K20 into K20H or K60 into K60H improves the capacitance. Nevertheless, the subsequent exchange procedures, which lead to samples K60(H)\(^2\) or K60HKH, though they lead to a drastic increase in the BET values and the water content does not bring any further capacitance improvement, and the best value remains that obtained for K60H. Similar observations, both for crys-
tallized compounds and amorphous ones, were made by Brousse et al. [45].

On the contrary, in the case of Na-derived sample, no capacitance increase is associated to the increase of the BET surface area. Moreover, in the case of Na60, the capacitance decreases after the proton exchange procedure which leads to an increase of the BET value.

These observations suggest that the BET surface area and the exact nature of the investigated phase (2D- or α-MnO2) are not the only parameters governing the capacitance, but that the morphology and the size of particles also play a determinant role. This conclusion agrees with general results of Toupin et al. [42], suggesting that in case of pseudocapacitive phenomena associated to faradic reactions the microstructure has a very important influence on capacitance values. In the case of exchanged potassium-containing samples, the morphology obtained with the mixture of rancieite and α-MnO2 phases should enable large capacities, but the subsequent complete transformation of rancieite into α-MnO2, which leads to an increase of the BET surface area, impedes the improvement of capacitive behaviour. Samples Na100, Na100H and Na100(H)2, which present a morphology and size particles comparable to K60H, also exhibit good capacitive properties, though they do not contain the α-MnO2 phase. It seems that in order to present high capacitance values, compounds must present in their morphology small blades (classified as SB-type morphology in Fig. 1). This observation emphasizes the drastic influence, even at low scan rate, of the microstructure on the capacitance, which is more important than the crystallographic structure in our case.

The cycleability of the different compounds was also studied, and curves presented in Fig. 11 for samples K60H (a), K60HKH (b) and Na100 (c) present an important decrease in capacitance when the scan rate increases. As described by Ardizzone et al. [83], at high sweep rates, the diffusion of cations is limited to the more accessible sites, called the “outer surface of the electrode”. In our case, the important decrease of the capacitance suggests that the extrapolated value at infinite sweep rate (corresponding to the “outer surface”) is very small. This is in accordance with a pseudocapacitive mechanism of charge storage, arising from faradic reactions sensitive to diffusion phenomena of the electroactive species (H+, alkali metal cation of electrolyte and/or manganese ions) into our bulk porous solid electrode material. Comparable decreases have been observed for similar compounds used under analogous conditions [40,41,45,48]. Fig. 11 shows that this effect is more important for the sodium-containing samples. At constant cycling rate, the cycleability depends also on the different compounds: for Na100, it is rather poor, with a capacitance fading exceeding 50%, from the 21st to the 50th cycle at 10 mV s\(^{-1}\), whereas for K60H and K60HKH the capacitance fading remains smaller than 20% in the same cycling range at similar cycling rates. This result is perhaps in accordance with assumptions of Brousse et al. [45], claiming that the presence of large tunnels in the crystallographic structure of α-MnO2 may increase reversibility by favouring intercalation of cations. It is also possible that in the case of Na100, the pseudocapacitive charge storage in the K\(_2\)SO\(_4\) electrolyte requires a H\(^+\)/Na\(^+\) exchange which is less favourable for the cycleability [77].

4. Conclusions

Nanostructured compounds of general formula K\(_x\)Mn\(_{3n}\)(\(1-x\))Mn\(_{IV}\)O\(_y\)O\(_z\)Mn\(_{VI}\)O\(_z\), with x = 0.37, 0.70 ≤ r ≤ 0.94 and 0.5 ≤ n ≤ 1.64, and exhibiting a rancieite-type structure, were prepared under mild conditions in aqueous solution. Subsequent proton- or alkali-ion-exchange reactions increase the surface areas of the products. In the case of potassium-containing compounds, the proton exchange leads to the α-MnO2 phase, with surface areas reaching 200 m\(^2\) g\(^{-1}\). Such products can be used in thick powder-based electrodes, leading to acceptable capacitances for a crystallized MnO2 compound. Very different results are obtained for compounds presenting just slight differences, and the best ones are not observed for a particular crystallographic structure, for a particular composition or for the highest surface areas, but depend on morphology and especially on the size of particles. The largest capacitances were obtained for Na100 and K60H. These two samples are made of agglomerates of spheres (0.5–1 μm in diameter) presenting an open texture similar to “sand-rose” with small blades of similar size. Nevertheless, the capacitance fading with both the increase of the cycling rate and the cycle number is less important for sample K60H, in which the open texture comprises blades and α-MnO2 sticks of comparable size.

Acknowledgment

Prof. Thierry Brousse (Laboratoire de Génie des Matériaux et des Procédés appliqués de l’ Ecole Polytechnique de l’Université de Nantes) is thanked for fruitful advices during this work.

References
