MnO$_x$/C composites as electrode materials. I. Synthesis, XRD and cyclic voltammetric investigation

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Abstract

MnO$_x$/C composite material was obtained by precipitation on suspended carbon black particles from dissolved KMnO$_4$. Doped composites were obtained by addition of Ca, Mg, Ni and other ions to the reaction mixture. The resulting solids are XRD amorphous or very poorly crystalline, but their chemical composition, Mn valence and electrochemical behaviour are very similar to those reported for birnessite, 7-A layered manganate(III,IV). We tested the electrochemical reduction/oxidation of the composite in 2 M KOH using cyclic voltammetry with three kinds of electrodes: microparticles immobilised on a carbon electrode (voltammetry of microparticles, vmp), carbon paste electrodes (cpee) and PTFE-bonded electrodes (tbe). Each technique has been used for its own merit: vmp is the best pilot technique, cpee enables fast quantification of the charge/mass relations, and tbe is the most reliable, but the slowest and the most laborious one. All the employed techniques yield directly comparable results. The composite can be discharged/recharged several tens of times at approximately 1 e$^-$/Mn efficiency. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: MnO$_x$/C composites; Electrodes; Cyclic voltammetry

1. Introduction

Manganese oxides are traditional materials used in primary Leclanché and also in commercially available secondary alkaline cells based on the procedure developed in the 1980s [1]. Several reports intimated that Mn oxides [2,3] could be employed as cheap, multifunctional electrocatalysts for the oxygen electrodes of fuel cells. The mentioned processes are based on several simple electrochemical reactions of Mn oxides, particularly on electrochemical redox cycling of Mn$^{IV}$/Mn$^{III}$/Mn$^{II}$, and possibly on chemical reactions of the reduced Mn species with oxygen.

Applicability of Mn oxides in the commercially available secondary alkaline cells is based on reactions with following features: the reactions are reversible, topotactic, and they consist of less than one-electron reduction of MnO$_2$ [1,4]. These reactions are performed in concentrated aqueous solution of KOH. Recently, a substantially different electrochemical system has been tested for possible application in secondary cells [5–9], which was reported to involve an almost complete, two-electron, heterogeneous reduction of manganese oxides, generally called ‘birnessites’, i.e. layered oxides with 0.7 nm interlayer spacing. This reaction is of a quite different nature, and it is performed in KOH solution [5–9] or in slightly acidic solution [10]. The theoretical description of the reduction of the layered Mn oxides and their reoxidation is insufficient. Contrary to the reactions of electrochemical manganese dioxide (EMD) or γ-MnO$_2$, the redox reactions of layered Mn oxides are enabled by the soluble Mn$^{III}$ hydroxocomplexes as intermediates [8].
We investigated in more detail a poorly crystalline Mn oxide obtained by impregnation of carbon black particles by permanganate aqueous solution, its synthesis and electrochemical properties were preliminarily reported in Ref. [3]. We focused on the phase composition of this composite, studied its cyclability in KOH solution and compared the results with those reported by others for birnessite electrodes. For electrochemical studies, we employed the technique of voltammetry of immobilised microparticles [11] as a fast qualitative analytical tool, which has been shown to be a fast technique suitable for testing electroactive materials [12,13]. We further employed the techniques of carbon paste electrodes and PTFE-bonded electrodes (tbe) for quantitative studies.

2. Experimental

Two kinds of carbon materials were used in this work. Carbon black Chezacarb SH (Chemapol Group, Czech Republic) was used as a support of MnO$_x$/C composite and also as a component of carbon paste electrodes. Chezacarb SH is hydrophilic carbon black designed as a sorbent for removing nonpolar substances from aqueous solutions. Its specific surface area is 1050 m$^2$/g. Acetylene black P-1024 (VEB Stickstoffwerk Pies-teritz, former East Germany) was used for the preparation of PTFE-bonded electrodes. It was produced formerly as an additive to Mn oxide electrodes of Leclanché cells. Its specific surface area is 74 m$^2$/g.

2.1. Synthesis of MnO$_x$/C composite and birnessites

2.1.1. Non-doped MnO$_x$/C

A 33 mmol sample of KMnO$_4$ was dissolved in 300 ml of water preheated to about 95°C. A suspension was prepared of 4 g carbon black and a solution of 10 mmol MnSO$_4$ in about 70 ml of water. The carbon black Chezacarb SH was wetted very quickly due to its hydrophilic nature. The suspension was poured into the hot permanganate solution, stirred, and then left to react on a hot plate at temperature close to a boiling point. The reaction started within several tens of seconds, and caused moderate evolution of gas, the increase in pH to about 8, and disappearance of the violet colour of permanganate ions. After several tens of minutes, the beaker with the suspension was removed from the hot plate and allowed to cool to room temperature for several hours. The solution above the suspension was pale yellow to yellow–brown. The suspension was then filtered, the solid washed with several portions of distilled water and dried at 110°C in an oven. The resulting composite consisted of Mn oxide and fine carbon powder and so it cannot be heated at too high temperatures without a risk of burning.

2.1.2. Me-doped MnO$_x$/C

A total of 33 mmol of KMnO$_4$ and 10 mmol of an appropriate Me-nitrate were dissolved in 300 ml of water preheated to about 95°C. A suspension of carbon black in a small amount of water was poured into the hot permanganate solution, stirred, and then left to react on a hot plate at a temperature close to the boiling point. The synthesis was finished as it was described above for non-doped MnO$_x$/C. Additions of Al, Ca, Co, Cu, Bi, Fe, Mg, Ni, Pb, Zn were tested, but only Ca, Mg, and Ni-doped composites were found to be worth further testing.

2.1.3. Birnessite

Birnessite samples were obtained by two different methods published in the literature. Bi-1 was obtained by mixing a 3% solution of hydrogen peroxide and 0.6 M NaOH with 0.3 M Mn(NO$_3$)$_2$ [15]. Bi-2 was obtained by sol–gel synthesis [16]. A 50 ml sample of 0.38 M KMnO$_4$ was mixed with 20 ml of 1.4 M glucose. The obtained gel was dried at 110°C following the procedure described in [16] and then heated at 400°C for 2 h. The resulting powder was suspended in hot water, filtered, washed with distilled water, and finally dried at 110°C.

2.2. Characterisation of MnO$_x$/C and birnessites

The phase composition of solids was checked using XRD (Siemens D5005, Germany). Chemical composition was determined after dissolution of solids in diluted HCl + H$_2$O$_2$ by chelatometric titration (Ca, Mg, Mn), AAS (Mn, Ni) and flame photometry (K). The redox stage of Mn was determined by iodometry, with potentiometric indication of equivalent point during back-titration of the evolved I$_2$ by Na$_2$S$_2$O$_3$.

2.3. Electrochemical experiments

Voltammetry of immobilised microparticles (vmp) was performed as already described [14]. A small amount of a dry sample was mechanically attached on the surface of paraffin-impregnated bar of spectral graphite. Such a working electrode, together with platinum counter electrode, and sce reference electrode were put to deaerated supporting electrolyte (2 M KOH). Voltammetric measurements were performed with a PC-controlled potentiostat (Autolab, Eco-Chemie, Utrecht, The Netherlands). Two measuring modes were employed: linear sweep voltammetry for cycling experiments and square wave voltammetry for studying the reversibility of the electrochemical reactions.

The same counter electrode and reference electrode, supporting electrolyte, and the electrochemical instrument was used for voltammetry with a carbon paste...
electroactive electrode (cpee). $\text{MnO}_x/C$ was mixed with carbon black, wetted with appropriate amount of 2 M KOH, and ground in an agate mortar to obtain paste with butter-like consistence. The paste was spread on a bar of spectral graphite and fixed by perforated PE foil, or the paste was pressed into a hole in the graphite bar and fixed by a cellulose seal. After finishing the experiments with carbon paste electrodes, the total amount of Mn was determined by AAS.

Voltammetry with PTFE-bonded electrodes was also used to simulate the electrodes in secondary cells. $\text{MnO}_x/C$ was well mixed with PTFE-coated acetylene black and the dry mixture was spread on a fine nickel mesh and pressed by a rolling machine. The obtained electrode was left to soak in supporting electrolyte (2 M KOH), and the voltammetric measurements were performed with Pt-counter electrode and $\text{Hg}/\text{HgO}$ reference electrode using a PC-controlled potentiostat (Autolab, EcoChemie).

3. Results and discussion

The composition of the Mn oxides synthesised is given in Table 1. As it follows from the chemical analysis, the Mn valence and K content in $\text{MnO}_x$ remarkably resemble that of birnessite, for which idealised formulas from $\text{Me}_1\beta\text{MnO}_2$, $\text{Me}_1\alpha\text{MnO}_2$ or $\text{Me}_1\beta\text{MnO}_2$, where Me is Na or K, were reported [21]. Accordingly, the sample Bi-1 has the empirical formula Na$_{1.3}$Mn$_{2.01}$. Na and K ions are placed in interlayer space and compensate the presence of Mn$^{II}$ and Mn$^{III}$ in the MnO$_2$ sheets of the birnessite structure. Because of ion-exchange properties of birnessite, the alkaline metals can be substituted by other metal ions, such as Mg$^{2+}$ and Ca$^{2+}$ [16,21]. Accordingly, we observed that the K/Mn ratio in $\text{MnO}_x/C$ (0.3) decreased in doped $\text{MnO}_x/C$ (0.1–0.2) in favour of the dopant ion. However, the amount of K together with the dopant ions exceeds that of idealised formulas of birnessites, and so we suppose, that a part of dopant ions can form grains or domains of a separate phase composition, such as $\text{CaCO}_3$ in Ca–$\text{MnO}_x/C$ according to XRD (see Table 1).

XRD revealed the diagnostic interlayer reflection typical for layered manganites only in the case of $\text{MnO}_x/C$, but the doped samples Me–$\text{MnO}_x/C$ yielded rather unclear XRD patterns (Fig. 1). Under the chosen synthetic conditions (permananate, slightly alkaline, slightly reducing environment, no particular ageing of the primary precipitate), one can expect the formation of layered manganites. We hence suppose that doped $\text{MnO}_x/C$ is an almost XRD amorphous birnessite-like phase. Synthetic birnessites Bi-1 and Bi-2 can be identified as turbostratic (t-Bi) and monoclinic (m-Bi) birnessites, respectively, according to diagnostic XRD lines reported in reference [21]. t-Bi occurs naturally and can be prepared by soft-synthetic methods, whereas m-Bi is easily obtained by ageing of t-Bi or by thermal decomposition of $\text{KMnO}_4$. Birnessites used for electrochemical studies usually belong among poorly crystalline, turbostratic, layered manganates [18–20]. m-Bi obtained by decomposition of $\text{KMnO}_4$ was also tested as an electrode for acidic secondary cells [10].

Cyclic voltammetry revealed surprising cycling stability of $\text{MnO}_x/C$, although birnessite and $\delta$-$\text{MnO}_2$ have been reported to be irreversibly reduced in alkaline medium [17] unless Bi is added to prevent the formation of inactive reaction products [5–7,18–20]. Cyclic voltammetric curves of immobilised $\text{MnO}_x/C$ and Ni–$\text{MnO}_x/C$ are shown in Fig. 2. Three or four cathodic peaks C and one or two anodic peaks A can be distinguished on the voltammetric curves. Their identification is complicated by the fact that the shape of the group of cathodic peaks C1–3 is very variable and changes with prolonged cycling. The same is true for the reoxidation peak A1, whose potential depends on the cycle number and which is sensitive to the potential range of the previous cathodic scan (see below).

The peaks C1–3, A1 and A2 are developed in voltammograms of all studied samples of $\text{MnO}_x/C$. The shape of these peaks is typical for each $\text{MnO}_x/C$ sam-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (wt.%)</th>
<th>K (wt.%)</th>
<th>Mn valence</th>
<th>Other metals (wt.%)</th>
<th>XRD a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-1</td>
<td>50.2</td>
<td></td>
<td>3.68</td>
<td>Na: 7.1</td>
<td>t-Bi</td>
</tr>
<tr>
<td>Bi-2</td>
<td>50.5</td>
<td>11.4</td>
<td>3.74</td>
<td>—</td>
<td>m-Bi</td>
</tr>
<tr>
<td>$\text{MnO}_x/C$</td>
<td>20.7</td>
<td>4.6</td>
<td>4.06</td>
<td>—</td>
<td>C</td>
</tr>
<tr>
<td>Ca–$\text{MnO}_x/C$</td>
<td>25.5</td>
<td>2.3</td>
<td>3.65</td>
<td>Ca: 4.0</td>
<td>C, c</td>
</tr>
<tr>
<td>Mg–$\text{MnO}_x/C$</td>
<td>20.8</td>
<td>1.4</td>
<td>3.65</td>
<td>Mg: 2.9</td>
<td>C</td>
</tr>
<tr>
<td>Ni–$\text{MnO}_x/C$</td>
<td>19.9</td>
<td>2.5</td>
<td>3.72</td>
<td>Ni: 6.8</td>
<td>β, C</td>
</tr>
</tbody>
</table>

* t-Bi, turbostratic birnessite; m-Bi, monoclinic birnessite; C, carbon (poorly developed); c, CaCO$_3$, calcite (PDF 5-586); β, β-NiOOH poorly developed (PDF 6-141).
The results obtained by the techniques employed is the change in the relative contribution of the peaks C1 and C2 to the reduction process and A1 and A2 to subsequent reoxidation. For example, the peaks C3 and A2 were almost suppressed in PTFE-bonded electrodes. We may conclude that the voltammetry of immobilised microparticles is the fastest technique, because the preparation of the working electrode takes several minutes. The carbon paste electrode is suitable for a quantitative analysis, because the total amount of Mn in each experiment can be easily controlled or determined after each experiment. PTFE-bonded electrodes are the best approach to the electrodes employed in batteries, and they are hence the most suitable for the study of the cycling stability of MnO$_x$/C electrode.

The cycling stability of MnO$_x$/C under conditions of voltammetry of immobilised microparticles is shown in Fig. 4, where the charge of the re-oxidation process A1 divided by the charge of the total reduction (C1 + C2) in the first scan (denoted as 1C) is plotted. That value $Q_{A1}/Q_{1C}$ usually increases during several cycles, reaches a flat local maximum and then it continuously decreases. In spite of these changes, it is obvious that the maximal re-oxidation charge is around the half of the charge of the total reduction of MnO$_x$/C in the first cycle. Assuming that the Mn valence in MnO$_x$/C is around 3.7 (Table 1) and that the total reduction of MnO$_x$/C leads to Mn II, the repeatable re-oxidation of the reduced form of MnO$_x$/C, Ca-MnO$_x$/C and Mg-MnO$_x$/C must involve approximately one electron per Mn atom.

To quantify the depth of discharge/recharge, i.e. to relate the charges of processes 1C and A1 to the actual total amount of Mn in the electrode, we employed techniques of carbon paste and PTFE-bonded electrodes (see Fig. 5). The carbon paste electroactive electrodes were prepared from birnessite, mixed with a ten-fold excess of carbon black, and from 1:1 weight mixture of MnO$_x$/C and carbon black. The total amount of Mn in the paste electrode was determined by AAS after each experiment. PTFE-bonded electrodes were prepared from a weighed amount of MnO$_x$/C. The results are summarised in Table 2 and they confirm the hypothesis that the first reduction of MnO$_x$/C represents almost total reduction to Mn II, whereas the further reduction processes C1 to C3 and reoxidation A1 involve an approximately one-electron reaction. This depth of discharge is somewhat smaller than approx. 1.3 e$^-$/Mn reported for Bi-birnessite [8], and approx. 1.6 e$^-$/Mn reported for chemically Bi-modified MnO$_2$ [5–7,9]. Under the same conditions, the reduction of non-substituted birnessite Bi-1 is only partial (see Table 2).

It is clear from the depth of the first reduction that it must formally be composed at least of two steps: Mn$^{IV}$/Mn$^{III}$ and Mn$^{III}$/Mn$^{II}$. There is a lack of description of
the reaction pathway and intermediates of the reduction of layered manganese oxides in literature, but it is clear that the reduction must involve some steps, although they might be overlapping. To separate them, we employed square-wave (sw) voltammetry of immobilised MnO$_x$/C to distinguish possible reversible and irreversible stages of the total reaction. The sw voltammograms showed in Fig. 6 reveal how complex is the reduction process. All studied doped and non-doped MnO$_x$/C produce curves similar to those of Ni-doped composite. There are two well developed peaks on the sw curve of Ni–MnO$_x$/C, denoted C1sw and C2sw. The former one corresponds to a hardly visible shoulder in linear sweep voltammogram, whereas the latter one corresponds to the major reduction peak C1. Both these processes responsible for the sw peaks are reversible, as follows from the shape of the curve of the backward current, which is almost mirroring the forward current. At the potential of the reduction peaks C2 and C3, there is at best only a trace of some process on sw curve in Fig. 6. This indicates that the processes C2 and C3 are very probably irreversible. Note that with birnessite Bi-I already the peak C2sw is also irreversible. Anodic sw voltammetric curves for Ni–MnO$_x$/C consist of several overlapping steps of a different degree of reversibility. The potentials of the sw reoxidation peaks are very different from the reduction ones, hence the complete reduction and oxidation is electrochemically irreversible. The peak A4sw is characteristic for Ni-doped composite and it corresponds to the Ni(OH)$_2$/NiOOH peak A3 in the linear sweep voltammogram of Ni–MnO$_x$/C (Fig. 2, right).

Because the first stage of the reduction of MnO$_x$/C seemed to be reversible up to a potential more positive than peak C1, we performed linear-sweep cyclic voltammetry in a restricted cathodic range to search for the corresponding anodic reaction. Examples of the voltammograms are given in Fig. 7. If the cathodic scan is finished immediately after the cathodic peak C1, reoxidation peak A1 shifts cathodically yielding peak A1’ and the separation of peaks C1/A1’ decreases to 0.09 V. A similar cathodic shift of reoxidation peak has already been reported for partly reduced chemically Bi-modified MnO$_2$ [8] and for Bi-birnessite in alkaline medium [19]. We may conclude that a certain reaction step of the overall reaction is very fast in comparison to solid-state transformations, such as γ-MnO$_2$ or EMD and their partly reduced products. According to the findings of Qu et al. [8], this fast step could involve reactions of dissolved intermediate [Mn(OH)$_6$]$^{3-}$ and their rate can hence be controlled by a relatively fast diffusion in liquid medium. A1’ could hence be a direct reoxidation of [Mn(OH)$_6$]$^{3-}$ to a Mn$^{IV}$ species,
whereas C2/C3 is a nucleation controlled formation of a solid phase of MnIII or the continuing reduction of MnIII to MnII. However, this explanation contradicts the total charges involved in electrochemical reactions (Table 2), which indicate that MnIV is not a dominant species during the prolonged cycling of MnOx/C.

The alternative explanation of the stepwise reduction/oxidation reactions can be based on the structural properties of birnessite [21] and on the study of the course of redox reactions of phyllosilicates [22]. MnIII and MnII cannot be present in any position in the MnO2 sheets of birnessite, but only in certain structural motives, such as MnIII or MnII-MnIII rich rows (every third one in the MnO2 sheet), or MnIII and MnII presented in interlayer space above and below ordered vacancies in the MnO2 sheets. One can hence assume that redox cycling of MnIII,IV layered manganates will involve transitions between certain metastable structures with corresponding average non-integer Mn valences. In these terms, the quasi-reversible peaks C1/A1 obtained in the limited potential range can represent a variation within an original birnessite-like structure, for example with every third row of Mn atoms occupied by MnII. The reduction step C1 (C2sw) can be followed by further reduction of MnIV atoms from the original MnO2 sheets and hence by an electrochemically irreversible transformation of the birnessite-like structure to another layered one, which is responsible for the irreversible peaks C2 and C3.

The voltammetric peaks of MnOx/C are in general sharper and better defined, and they occur at more negative potentials in comparison with poorly defined diffusion waves usually obtained by cyclic voltammetry of γ-MnO2 or EMD [12,13,17]. The peak potentials obtained by voltammetry of immobilised MnOx/C are given in Table 3. The potentials and the peak shapes are comparable with those reported in literature for layered Mn oxides [9,19,20]. For example, the peaks C1 and C2 of MnOx/C are undoubtedly identical to the characteristic double-peak reported in literature for the deeply discharged–charged manganese oxides [9,19,20]. Similarly to reported layered Mn oxides, MnOx/C can also be discharged/recharged, although the number of cycles is, at present, of the order of only several tens. This may seem much less than several hundreds of cycles obtained with the Bi-doped layered oxides [5–7], however, it has been believed that only Bi is able to prevent the formation of non-electroactive reaction by-products [23]. On the basis of our findings, we can propose an alternative explanation: the presence of

**Table 2**

Voltammetry of carbon paste electroactive electrodes (cpee) at scan rate 1 mV/s and PTFE-bonded electrodes (tbe) at 10 mV/s

<table>
<thead>
<tr>
<th>Sample (technique)</th>
<th>1C (e^-/Mn)</th>
<th>A1MAX (e^-/Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-1 (cpee)</td>
<td>Low</td>
<td>0.3</td>
</tr>
<tr>
<td>MnOx/C (tbe)</td>
<td>p.d. b</td>
<td>0.7</td>
</tr>
<tr>
<td>Ca-MnOx/C (cpee)</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Mg-MnOx/C (cpee)</td>
<td>1.6</td>
<td>1.1</td>
</tr>
<tr>
<td>Ni-MnOx/C (tbe)</td>
<td>p.d.</td>
<td>1.0</td>
</tr>
<tr>
<td>Ni-MnOx/C (cpee)</td>
<td>1.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a Charges are compared to the total amount of Mn. 1C: the charge of the first cathodic process, A1MAX: the maximal charge of the anodic peak A1.

b p.d., poorly defined voltammetric peak to subtract the background current.
crystallisation nuclei of layered manganates that scavenge the soluble Mn$^{III}$ and Mn$^{II}$ intermediates and hence prevent the formation of the non-electroactive Mn$_3$O$_4$, which is the most stable low-valence Mn oxide in aqueous environment. Maybe the layered structure is preserved during the almost complete reduction of MnO$_x$/C as discussed above.

4. Conclusion

The XRD amorphous composite material, obtained by chemical reaction of aqueous solution of KMnO$_4$ with suspended carbon black, has a composition and electrochemical properties very similar to the layered Mn oxides, which are usually denoted birnessites in
Table 3

Potentials of linear-sweep voltammetric peaks of immobilised MnO\textsubscript{x}:C and the results published for Bi-birnessites \textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample denotation</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>A1</th>
<th>A2</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-1</td>
<td>−0.21</td>
<td>−</td>
<td>−</td>
<td>0.08</td>
<td>−</td>
<td>2 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>MnO\textsubscript{x}:C</td>
<td>−0.17</td>
<td>−0.3</td>
<td>−0.55</td>
<td>0.14</td>
<td>0.64</td>
<td>2 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>Ca–MnO\textsubscript{x}:C</td>
<td>−0.21</td>
<td>−0.3</td>
<td>−0.47</td>
<td>0.13</td>
<td>−</td>
<td>2 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>Ni–MnO\textsubscript{x}:C</td>
<td>−0.23</td>
<td>−0.3</td>
<td>−</td>
<td>0.02</td>
<td>−</td>
<td>2 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>Bi-birnessite</td>
<td>−0.28</td>
<td>−0.36</td>
<td>−</td>
<td>−0.09</td>
<td></td>
<td>9 M KOH</td>
<td>[5,6]</td>
</tr>
<tr>
<td>Bi-doped MnO\textsubscript{2}</td>
<td>−0.30</td>
<td>−0.34</td>
<td>−</td>
<td>−0.16</td>
<td>0.19</td>
<td>9 M KOH</td>
<td>[9]</td>
</tr>
<tr>
<td>Bi-birnessite</td>
<td>−0.24</td>
<td>−0.32</td>
<td>−</td>
<td>0.23</td>
<td>0.40</td>
<td>1 M KOH</td>
<td>[20]</td>
</tr>
<tr>
<td>Ni–MnO\textsubscript{x}:C</td>
<td>−0.23</td>
<td>−0.3</td>
<td>−</td>
<td>−0.16</td>
<td>0.19</td>
<td>9 M KOH</td>
<td>[9]</td>
</tr>
<tr>
<td>Bi-birnessite</td>
<td>−0.30</td>
<td>−0.34</td>
<td>−</td>
<td>−0.16</td>
<td>0.19</td>
<td>9 M KOH</td>
<td>[9]</td>
</tr>
<tr>
<td>Bi-doped MnO\textsubscript{2}</td>
<td>−0.30</td>
<td>−0.34</td>
<td>−</td>
<td>−0.16</td>
<td>0.19</td>
<td>9 M KOH</td>
<td>[9]</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Potentials referred to she. Peak denotation according to Fig. 2.

electrochemical literature. The composite can be discharged and recharged several tens of times in KOH solution with approximate depth of discharge of one electron per Mn atom. Among the studied substituted composites, especially Ni-doped samples show the best cycling stability in PTFE-bonded electrodes. This stability is not improved by higher-valent metal dopants, such as Bi, Ph, or Ti, which are usually used to increase the cyclability of Mn oxides, but most likely by the poor crystallinity of the composite and by its particular nano-crystalline layered structure.

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References