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MnO₂-MXene composite as electrode for supercapacitor

Yachao Zhu,^{1,2,3} Khalil Rajouâ,^{1,3} Steven Le Vot,^{1,3} Olivier Fontaine,^{4,5} Patrice Simon,^{2,3} and Frédéric Favier^{1,3}

1. Institut Charles Gerhardt Montpellier (ICGM), Univ. Montpellier, CNRS, ENSCM, Montpellier, France
2. CIRIMAT, Université de Toulouse, CNRS, INPT, Université Paul Sabatier, 118 route de Narbonne, 31062, Toulouse, France
3. Réseau sur le Stockage Electrochimique de l'énergie (RS2E), FR CNRS 3459, France
4. School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong, 21210, Thailand
5. Institut Universitaire de France, 75005 Paris, France

email : frederic.favier@umontpellier.fr

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ABSTRACT: A MnO₂-MXene composite material is reported, in which MnO₂ particles have been grown onto Ti₃C₂ MXene flakes. Thanks to its interconnected structure, it can not only boost the low electrical conductivity of MnO₂, but also suppress the restacking of MXene flakes. As an electrode material in a three-electrode cell, the composite showed greater capacitance and improved stability performance than raw MnO₂ in both KOH and Na₂SO₄ aqueous electrolytes. Equipped with MnO₂-MXene composite material as positive and activated carbon as negative, an asymmetric device using Na₂SO₄ as electrolyte displayed an energy density of 20 Wh kg⁻¹ at 500 W kg⁻¹ power density. On the other hand, the device operated in KOH electrolyte showed an energy density of 17 Wh kg⁻¹ at 400 W kg⁻¹, and 11 Wh kg⁻¹ at 8 kW kg⁻¹.

INTRODUCTION

Supercapacitors (SCs)¹, including electrochemical double-layer capacitors (EDLCs)² and redox-based pseudocapacitors³, have been extensively studied as promising and efficient candidates for energy storage systems thanks to many attractive features that advantageously supplement those of batteries⁴. These include high power density, fast charge-discharge rate and long cycle life^{5,6}. In contrast, their energy density is lower. Carbon-based EDLCs⁷ usually show a high rate capability thanks to their electrostatic charge storage mechanism based on the reversible adsorption-desorption of electrolytic ions onto the large surface area of the electrode material during quick charge-discharge processes⁸. Various materials such as porous carbons⁹⁻¹⁴ and graphene¹⁵⁻¹⁷ have been explored as

electrode materials and the vast majority of the supercapacitors commercialized worldwide are activated carbon -based EDLC devices. On the other hand, oxide-based pseudocapacitive materials¹⁸ store charges through fast and reversible redox reactions near the surface of the material, leading to attractive capacitances^{19,20}. In comparison with EDLCs, energy density is greater thanks to the Faradaic contribution but because of the kinetics of the involved redox reactions (intrinsically slower than electrosorption), power is less attractive. Many metal oxides such as RuO₂²¹⁻²⁴ and MnO₂²⁵⁻²⁷ have been confirmed as suitable pseudocapacitive electrode materials. The impact on the storage performance of both electronic and crystallographic structures of the oxides has been demonstrated.²⁸⁻³² As an example, storage performance, including rate capabilities, has been demonstrated to depend on the structure of the pseudocapacitive oxide. This is especially true with MnO₂ polymorphs built on 1 to 3D structures, either on channeled, layered or compact arrangements allowing the more or less efficient solid-state diffusion of compensating cations involved in the charge storage mechanism.³⁵⁻³⁸ On the other hand, the poor intrinsic electronic conductivity of MnO₂ limits its overall rate capability, which inhibits the electrode capacitance to reach the theoretical value at ~1380 F/g.^{33,34} As such, improving the electronic conductivity of MnO₂-based electrode materials remains a consistent strategy to reach greater performance, especially rate capability, and, consequently, greater device power.

Recently, two-dimensional transition metal nitrides/carbides (MXenes)^{39,40} have been successfully prepared by etching of A layers from MAX phases, giving a few atoms thick layered extended family with a general formula $M_{n+1}X_nT_x$, where M represents a transition metal, X is C and/or N, and T_x stands for surface terminations⁴¹⁻⁴³. Thanks to their high accessible surface areas promoted by a 2D structure as well as the high electrical conductivity of the carbide-core layer ($\sim 4,000 \text{ S.cm}^{-1}$), MXene materials can achieve attractive electrochemical performance in aqueous electrolytes, with capacitances beyond 250 F g^{-1} or $1,500 \text{ F.cm}^{-3}$ ⁴⁴⁻⁵⁰.

Back in 2016, Rakhi et al has reported on the synthesis and electrochemical characterization of MnO_2 nanowhiskers on MXene surfaces⁵¹. This is the ϵ form of MnO_2 , also known as MnO_2 Ramsdelite, which was actually precipitated at the surface of exfoliated flakes of Ti_3C_2 . The Ramsdelite structure is built on edge-sharing MnO_6 octaedra in a 1x2 configuration forming channels in which alkali cations are stabilizing the structural arrangement, Therefore, its 1D structure provides ϵ - MnO_2 with a fair ionic conductivity and, consequently, a pseudocapacitive behavior in neutral aqueous electrolytes with fair charge storage capabilities when used as electrode material in a supercapacitor⁵². As such, these authors claimed up to 212 F g^{-1} capacitance (at 1 A g^{-1} current density) could be obtained with an electrode based on the prepared ϵ - $\text{MnO}_2/\text{Ti}_3\text{C}_2$ composite cycled in a 30wt% KOH electrolyte. Despite this attractive performance and the elegance of the synthetic approach, there is still room for improvement. This, especially by considering more performing MnO_2 polymorphs to decorate the Ti_3C_2 MXene flakes. This could be MnO_2 birnessite, or δ - MnO_2 , which has shown, thanks to its more open 2D layered structure, up to twice the capacitance, as electrode material, than that of Ramsdelite⁵². Rakhi et al choose to use a symmetric two electrode setup while an asymmetric device with an activated carbon negative electrode, for example, would have been more realistic to discuss power and energy densities. Moreover, they limited their study to a single KOH based electrolyte while MnO_2 , as a pseudocapacitive electrode material, is known to show enhanced electrochemical performance when operated in safer neutral sulfate or nitrate -based aqueous electrolytes.^{53,54,55,56} Data in Table S1 and associated references are supporting these observations. With the objective to select a more performing MnO_2 material to be incorporated in a nanocomposite with Ti_3C_2 MXene, we initially studied changes in the crystalline structure of MnO_2 and associated electrochemical performance, correlated with the preparation temperature. Interestingly, when increasing the temperature, a material based on layers (δ - MnO_2) together with fibers (α - MnO_2) was obtained, showing an attractive cooperative electrochemical behavior taking advantage of the greater capacitance from the δ phase and greater rate capability from the α phase. Furthermore, exfoliated MXene was used to prepare a composite material in which MnO_2 particles were grown, at the selected temperature, on MXene flakes providing an improved conductivity and preventing the restacking of MXenes layers. Thanks to these advanced features, the MnO_2 eMXene (MeM) composite electrode was first evaluated in terms of specific capacitance, rate and cycling capabilities either in KOH and Na_2SO_4 electrolytes. The composite and activated carbon were used

as positive and negative electrode, respectively, to fabricate an asymmetric device. Thanks to the large potential window of 2V in Na₂SO₄, AC//MeM-Na device showed attractive energy and power densities. In KOH electrolyte, AC//MeM-K device showed slightly lower but fair energy and power performance.

MATERIALS AND METHODS

Preparation of Ti₃C₂ MXene suspension and film

1 g of LiF and 20 mL of 9 M HCl were mixed and stirred in a plastic bottle. After a few minutes, 1 g Ti₃AlC₂ grey powder was progressively added to the mixture. This etching process was kept at 35 °C for 24h under constant stirring. Accordingly, Ti₃C₂ MXene flakes were repeatably rinsed off by ultrapure water to rise the pH of the effluent up to about 6. After re-dispersing MXene flakes in 250 mL pure water, the flakes were exfoliated by sonication for one hour. The un-exfoliated Ti₃C₂ material was removed by centrifugation for 1 h. Finally, a Ti₃C₂ MXene suspension was obtained. The MXene film was prepared by an easy one-step method. In more details, a given mass of MXene suspension in water was slowly filtered on a PTFE membrane under vacuum. The resulting Ti₃C₂ MXene film was dried in a glass tube under vacuum before use.

Preparation of MnO₂ by co-precipitation

0.1272 g MnCl₂ and 0.24 g KMnO₄ were respectively dispersed in ultra-pure 20 mL H₂O under constant stirring. Then, the KMnO₄ solution was added drop by drop to the MnCl₂ solution (5 minutes duration operation). The resulting suspension was transferred in a laboratory reflux apparatus and heated at a 120 °C setpoint temperature for 6 h. After filtration, collected brown MnO₂ powders were dried at 80 °C in air. Additionally, the effect of the co-precipitation temperature was investigated and syntheses were conducted at 30, 80, 140 °C setpoint temperatures. Corresponding samples are referred as M-30, M-80, M-120 and M-140 depending on the temperature the powder was prepared.

Preparation of MnO₂@MXene

20 mL of a mixture with 20.0 mg Ti₃C₂ MXene and 127.2 mg MnCl₂ was first prepared. Using the procedure as described above for the preparation of raw MnO₂, 20 mL KMnO₄ solution was slowly added and the resulting suspension was kept at a temperature of 120 °C, for 6 h. This synthesis temperature was chosen for reasons explained below. After drying, the MnO₂@MXene composite material was obtained.

XRD, SEM, TEM sampling and equipment

X-ray diffraction patterns of the prepared materials were obtained using a Phillips X'Pert diffractometer with Cu K α radiation ($\lambda=1.5405\text{\AA}$) in a Bragg-Brentano configuration. A JEOL JSM-6300F scanning electron microscope (SEM) was used to investigate the powder morphologies.

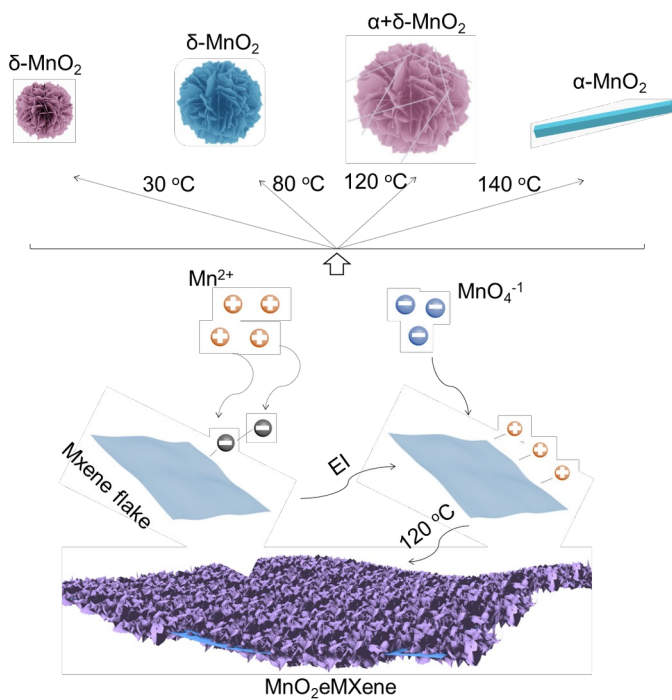
Sampling was done on dry powders on carbon tape. Energy-dispersive X-ray spectroscopy (EDX) and mapping in SEM was applied to analyze elemental compositions and distributions. Transmission electron microscopy (TEM) measurements were done using a JEOL 1200EX2 TEM instrument. Sampling was done on carbon-copper grids.

Electrochemical characterization

A VMP3 multi-channel Bio-Logic electrochemical workstation was used for all the electrochemical measurements done at controlled room temperature (23 °C) in a three-electrode configuration as well as in a Swagelok setup. Electrode discs were fabricated by first mixing the prepared materials (60%), acetylene black (30%) and PTFE (10%) in ethanol. The resulting paste was then rolled as a film, finally cut as 8 mm diameter round samples using a puncher tool. In the three-electrode setup, the working electrode was the synthesized materials, the reference electrodes were Hg/HgO (KOH) and Ag/AgCl (Na₂SO₄), and the counter electrode was a platinum foil. Gravimetric capacitances were normalized to the active material weight. The mass loadings of pure MnO₂ are given in Table S2. The weight loadings of composite are about 6.0 mg cm⁻². In the asymmetric device, a commercial activated carbon (PICA) was used as negative electrode. Electrode mass balancing was done by considering capacitances calculated from CVs done on individual electrodes in selected electrolytes.

RESULTS AND DISCUSSION

MnO₂ powders were prepared by a co-precipitation method using Mn²⁺ and MnO₄⁻¹ as reductant and oxidant, respectively (Figure 1, top). Depending on the synthesis temperature (from 80 to 140 °C), resulting MnO₂ materials exhibited some discrepancies in their crystalline structure from δ to α phase, additionally following morphological changes from nano sheets to nano fibers. Furthermore, Ti₃C₂ MXene flakes were used as substrates to grow MnO₂ by the same co-precipitation method at a synthesis temperature of 120 °C, eventually resulting in a nanostructured MnO₂eMXene composite (Figure 1, bottom).



EI: electrostatic interaction

Figure 1. Schematic diagram of material preparations.

Structural changes in MnO_2 powders induced by the selected preparation temperature have been evidenced by XRD measurements (Fig. S1). For MnO_2 -30 (black), MnO_2 -80 (grey) and MnO_2 -120 (blue) samples, corresponding to MnO_2 powders prepared at 30, 80 and 120 °C, respectively, diffraction peaks are indexed and correspond to δ - MnO_2 (Birnessite, JCPDS 1098^{57,58}). This manganese dioxide morphotype shows a layered structure built on 2D layers of edge-sharing $[\text{MnO}_6]$ octahedra. Whereas, a clear difference in the crystal structure is distinctly revealed in the XRD pattern of the MnO_2 -140 sample, prepared at 140 °C. It exhibits a series of new peaks as well as the absence of the (001) peak previously at $66.28^\circ 2\theta$. This pattern matches that of α - MnO_2 (Hollandite, JCPDS 44-0141) whose structure is built on 1D tunnels (2x2 edge-sharing MnO_6 octahedra). A closer look at the MnO_2 -120 XRD pattern also shows some extra peaks of lower intensity, especially at $56.21^\circ 2\theta$ which corresponds to the (600) diffraction peak of the α -type structure. This latter suggests a mixture, mostly made of δ - MnO_2 and some α - MnO_2 , to be obtained at 120 °C.

As the reaction temperature was increased, the powder morphologies evolved consistently with the structural changes pointed out by XRD analysis. The micro-morphology of prepared powders was studied by scanning electron microscopy measurements. In Fig. S2, the expected δ - MnO_2 “sand rose” morphologies are clearly observed in MnO_2 -30 and MnO_2 -80. These roughly spherical particles are made of disordered aggregated MnO_2 platelets. In contrast, at 140 °C, α - MnO_2 nano-rods and needles are mostly observed, together with a few “sand rose” particles. Finally, as suggested by XRD analysis, MnO_2 -120 sample is confirmed as a mixture of both types of δ - MnO_2 and α - MnO_2 nano-crystals.

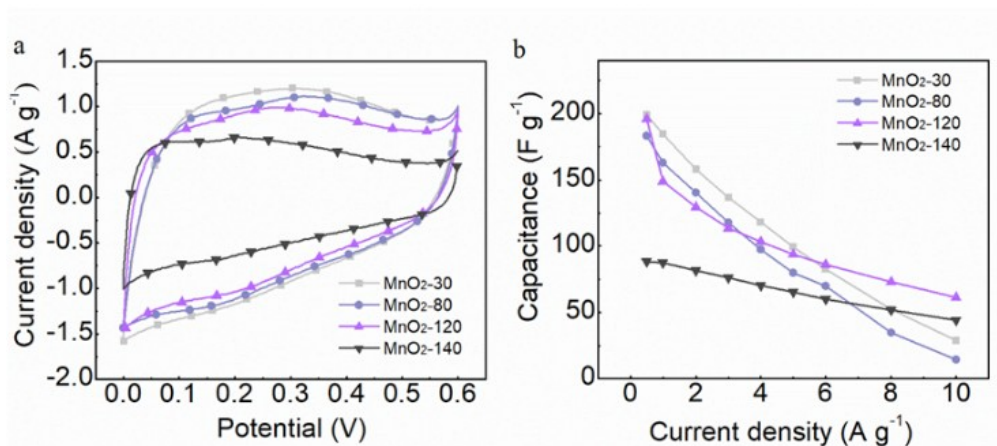


Figure 2. Electrochemical performances comparison of MnO₂ prepared at various reaction temperatures in 1 M KOH. (a) Cyclic voltammetry curves at 5 mV s⁻¹ scan rate. (b) Comparison of specific capacitances from galvanostatic measurements at various current densities.

Electrodes based on the prepared MnO₂ materials were tested in a three-electrode setup in 1 M KOH electrolyte with the objective to evaluate the impact of their structure/morphology on their electrochemical behavior. Corresponding capacitances were calculated from cyclic voltammetry measurements at 5 mV s⁻¹ scan rate from 0 to 0.6 V versus Hg/HgO reference electrode (Fig. 2a). Capacitances are detailed in Table S1 but a direct observation of the CV areas allows to compare the various electrode material performance: MnO₂-30 electrode CV displays the largest area in the series and correspondingly, the greatest capacitance at 181 F g⁻¹. As the synthesis temperature was increased, the capacitance of the resulting material decreased, and MnO₂-140 showed the lowest capacitance in the series at 98 F g⁻¹. This trend is assigned to the structural characteristics of the prepared MnO₂. δ -MnO₂ 2D structure has been shown to be highly favorable to the diffusion in between MnO₂ layers of electrolytic cations involved in the charge storage mechanism. As such, corresponding capacitances are the greatest in the MnO₂-based electrode material family⁵². In contrast, α -MnO₂ built on more constraining 1D tunnels is less performing either in terms of ionic conductivity and capacitance.⁶² Measured electrode capacitances are actually related to the δ -MnO₂/ α -MnO₂ composition ratio. They decrease as the α -MnO₂ content increases while increasing the synthesis temperature. Capacitances were measured at various charge-discharge rates by galvanostatic measurements (Fig. 2b). Similarly, to CV measurements, it was found that, at a low current density such as 0.5 A g⁻¹, MnO₂-30 and MnO₂-80 electrode materials, mostly composed of δ -MnO₂, showed larger capacitances than α -MnO₂-rich material such as MnO₂-140. However, capacitances of MnO₂-30 and MnO₂-80 quickly decreased as the current density was increased. For example, the capacitance of MnO₂-30 -based electrode was 29 F g⁻¹ and that of MnO₂-80 was 14 F g⁻¹ at 10 A g⁻¹. The rate capabilities of these electrodes are as such, fairly limited. In contrast, while the capacitance of MnO₂-140 was limited to 88 F g⁻¹ at 0.5 A g⁻¹, it was still 44 F g⁻¹ at 10 A g⁻¹. Finally, not only could MnO₂-120 electrode deliver a high capacitance of 196 F g⁻¹ at 0.5 A g⁻¹, but it also retained a 62 F g⁻¹ capacitance at 10 A g⁻¹. This latter electrode behavior can be explained by

its specific composition based on a mixture of δ - and α - MnO_2 . At low current density, δ - MnO_2 provides the electrode with its attractive low rate capacitance assigned to its 2D open structure and associated fair ionic conductivity, while α - MnO_2 component favorably contributes to the capacitance at high current density thanks to its greater electronic conductivity.⁵² Thanks to this peculiar composition in the series, MnO_2 -120 electrode material offers the best compromise in terms of rate capabilities, with enhanced capacitances in a wider range of charge-discharge regimes. Because of these well balanced electrochemical properties, 120 °C synthesis temperature was chosen for the preparation of $\text{MnO}_2/\text{MXene}$ composite based on the precipitation of MnO_2 at the surface of exfoliated Ti_3C_2 MXene flakes.

X-ray diffraction (XRD) patterns of the prepared raw MnO_2 -120 and $\text{MnO}_2/\text{MXene}$ composite materials are depicted in Figure 3. As expected, MnO_2 powder prepared at 120 °C corresponds to the above described mixture made of δ - MnO_2 (mainly) and some α - MnO_2 . The XRD pattern of the Ti_3C_2 MXene shows the usual features of restacked 2D materials with a series of diffraction peaks of decreasing intensity at greater diffraction angle. These correspond to the (002n) atomic layers of Ti_3C_2 MXene and are consistently measured at angles corresponding to the interlayer distance. The XRD pattern of the composite material obtained by precipitation of MnO_2 in presence of exfoliated Ti_3C_2 MXene layers at 120 °C retains the characteristics of the poorly crystallized MnO_2 -120 material. Actually, only remain the main peaks from the pristine MnO_2 . In contrast, the intense 002 peak of the MXene component almost completely vanishes. This is a proof that this synthetic method prevents exfoliated MXene layers to restack in the composite. This XRD analysis suggests that δ - MnO_2 actually grows at the surface of Ti_3C_2 MXene flakes made of a very few layers of Ti_3C_2 . Moreover, a tendency of the MnO_2 layers to grow parallel to those of MXene is supported by the greater intensity of the (111) peak, characteristic of a preferential orientation of the MnO_2 layers in the composite.

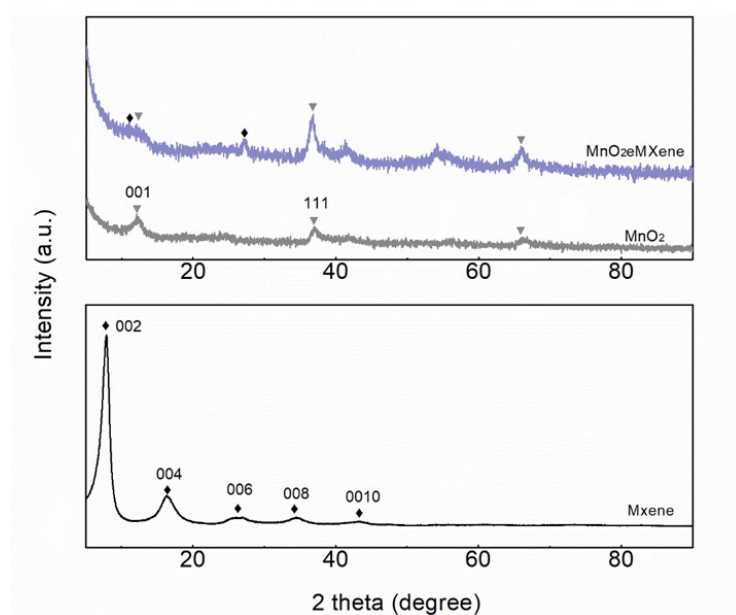


Figure 3. XRD patterns of MXene, δ - MnO_2 and $\text{MnO}_2/\text{MXene}$ composite.

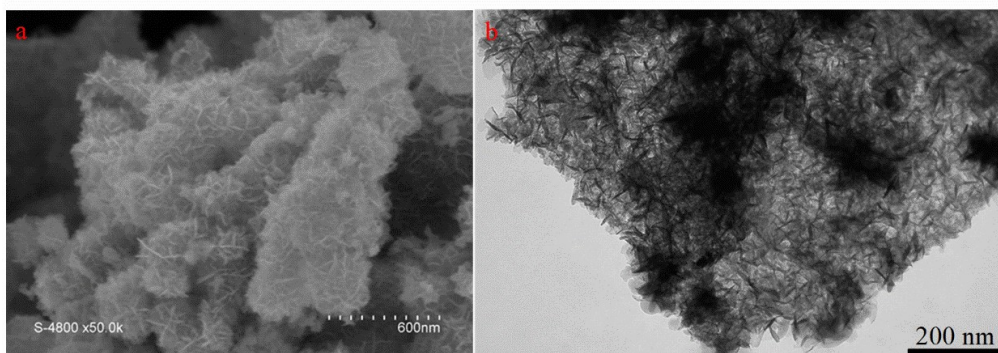


Figure 4. SEM and TEM images of MnO₂/MXene composite.

When MXene flakes are introduced as substrates in the synthetic medium, Mn²⁺ cations are first adsorbed on negatively charged MXene layers⁵⁹⁻⁶¹ by electrostatic interactions. Mn²⁺ adsorption is self-limited as it stops when all the Ti₂C₃ flake negative charges are counter-balanced. By reacting with MnO₄⁻ anions at 120 °C, MnO₂ particles gradually and uniformly grow on the flat MXene template. The resulting material morphology can be evidenced by SEM and TEM imaging. From SEM image in Figure 4a, it is difficult to assign any morphology difference between the composite and raw MnO₂ (see Fig. S2c for comparison with MnO₂-120). Moreover, it was not possible to identify anything looking like the pristine Ti₃C₂ MXene flakes in the micrographies. At this stage, we argue this is because they are fully covered by MnO₂ particles. TEM image in Figure 4b is more indicative as it shows a rather homogeneous thick layer of MnO₂ grown at the surface of a micro-sized Ti₃C₂ MXene flake. The same morphology was found all over the analyzed sample and, either by SEM or TEM, it was not possible to identify any small or individual MnO₂ particles nor individual Ti₃C₂ MXene flake neither uncovered nor partially covered by MnO₂ particles. Consistently, EDX mappings shown in Figure S6 demonstrates the homogeneous distribution of the various components Mn, O, Ti and C, all over the surface of the sample, characteristic of an intimate mixture of MnO₂ and Ti₃C₂ MXene in the composite and confirming the preferential growth of MnO₂ particles at the surface of MXene flakes. Consistently with the self-limited adsorption of Mn²⁺ cations at MXene surface, the same composition was found on every spots analyzed by EDX mapping. EDX analysis (Table S2) also evidenced the presence of K in the composite, as expected intercalated cations in between the layers of δ-MnO₂. As suggested by the SEM images, MnO₂ appears as the predominant component while Ti₃C₂, underneath the MnO₂ thicker layer, is more difficult to accurately detect and analyze.

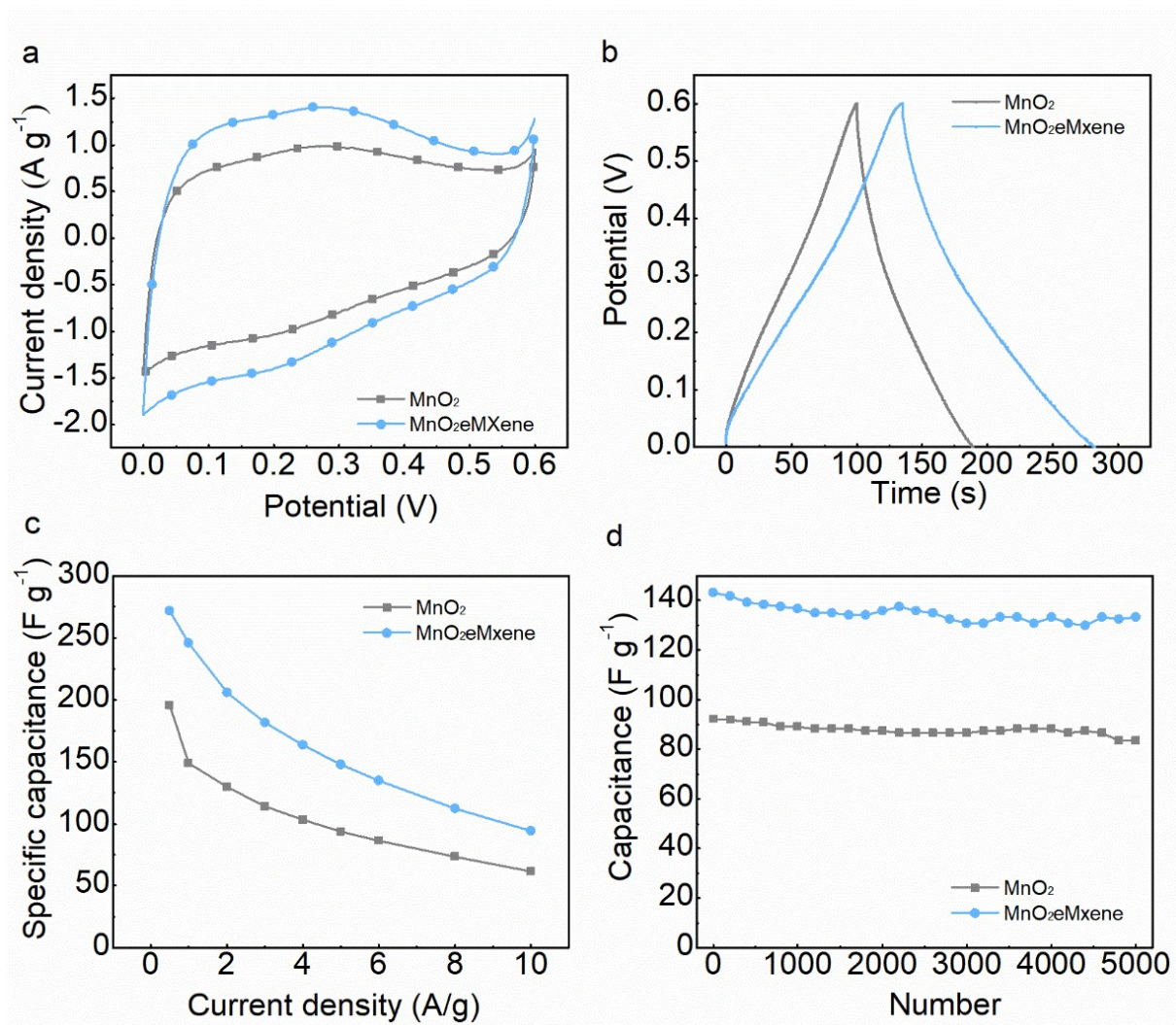


Figure 5. Electrochemical characteristics of MnO₂eMXene composite and MnO₂-120 -based electrodes in 1 M KOH electrolyte. (a) Cyclic voltammety measurement at 5 mV s⁻¹ scan rate. (b) Galvanostatic charge-discharge curves at 1 A g⁻¹ current density. (c) Comparison of specific capacitances from galvanostatic measurements at various current densities. (d) Cycling capability over 5k charge-discharge cycles at 5 A g⁻¹.

MnO₂-120 and MnO₂eMXene -based electrodes were used for electrochemical characterization in a three-electrode setup in KOH as well as in Na₂SO₄ electrolytes. In 1M KOH, cyclic voltammograms measured at 5 mV s⁻¹ between 0 and 0.6 V versus Hg/HgO reference electrode in Figure 5a are characteristic of a pseudocapacitive electrode material. These CVs, but also the corresponding galvanostatic curves in the same potential range (Fig. 5b), show that the composite displays a greater capacitance than MnO₂-120 electrode. However, both electrode materials have similar rate capabilities (Fig. 5c). As such, the composite can deliver a capacitance of 272 F g⁻¹ at 0.5 A g⁻¹, fairly more than MnO₂-120 at 196 F g⁻¹ at the same current density, that decreases by 55 % down to 148 F g⁻¹ at 5 A g⁻¹. For MnO₂-120 electrode, the capacity loss at 5 A g⁻¹ is of 47 % at 94 F g⁻¹. As anticipated, the MnO₂eMXene -based electrode inherits the rate capability of MnO₂-120 demonstrated above. On the other hand, the composite capacitance at 5 A g⁻¹ is 133 F g⁻¹ after 5k

charge-discharge cycles, corresponding to 93% of its initial capacitance (Fig. 5d). Conversely, the capacitance of MnO₂-120 electrode at 83 F g⁻¹ after the same electrochemical cycling program is characteristic of a 90% retention, about the same as using the MnO₂eMXene composite electrode. Electrochemical characteristics of the prepared electrode materials were also tested in sodium sulfate electrolyte. Results are shown in Figure 6. Here again, both MnO₂-120 and MnO₂eMXene -based electrode CVs show roughly rectangular shapes (Fig. 6a) while usual triangular galvanostatic responses are obtained (Fig. 6b). Corresponding capacitances were calculated at various current densities by galvanostatic cycling (but also from CVs at various scan rates in Figure S7 and Table S3). For MnO₂-120 electrode, the capacitance is 114 F g⁻¹ at 0.5 A g⁻¹ but fades down to 8 F g⁻¹ at 10 A g⁻¹, demonstrating the poor rate performance (7%) usually observed for MnO₂-based electrodes in neutral electrolyte.^{55,56,62} Oppositely, at higher current, the electrode made of MnO₂eMXene composite can hold almost 50% of its low current capacitance, delivering 165 F g⁻¹ (0.5 A g⁻¹) and 81 F g⁻¹ (10 A g⁻¹) (Fig. 6c). In neutral electrolyte, the greater rate capabilities of MnO₂eMXene can hardly be assigned to some α -MnO₂ contribution as in KOH electrolyte for two reasons. Firstly, the rate capability of α -MnO₂ has been shown to be very limited in Na₂SO₄ 1M.⁶² Secondly, despite the same synthesis temperature, there is not much evidence of any needle in the SEM/TEM micrographies of MnO₂eMXene composite or α -MnO₂ diffraction peaks in its XRD pattern. The enhanced rate performance of MnO₂eMXene should be assigned to the enhanced electronic conductivity thanks to the MXene component. The cycling capability over 5k cycles was evaluated at 5 A g⁻¹ current density (Fig.6d). For both prepared electrode materials, there is not any noticeable capacitance fading, demonstrating the good stability of these pseudocapacitive materials upon cycling at this quite realistic regime (from 40 to 60 sec. for a complete charge discharge cycle). At this stage, the contribution of the MXene core to the cycling capability of composite electrodes could not be assessed as, either in KOH or Na₂SO₄ electrolytes, capacitance retention of MnO₂ and MnO₂eMXene -based electrodes remained close to 100 % after 5k charge-discharge cycles.

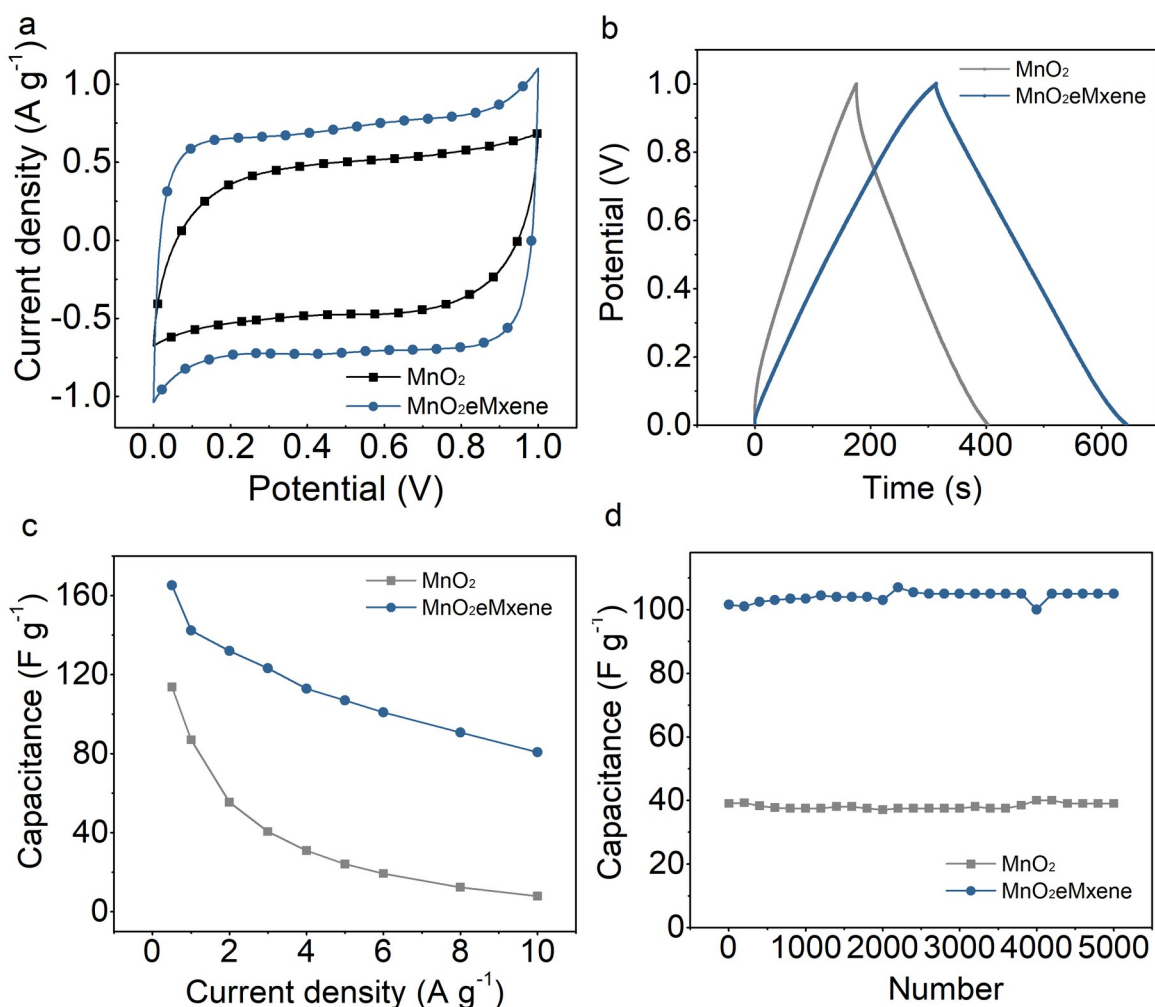


Figure 6. Electrochemical characteristics of of $\text{MnO}_2\text{eMXene}$ composite and $\text{MnO}_2\text{-120}$ -based electrodes in 1 M Na_2SO_4 electrolyte. (a) CV curves at 5 mV s^{-1} scan rate. (b) Galvanostatic charge discharge curves at 0.5 A g^{-1} current density. (c) Comparison of specific capacitances from galvanostatic measurements at various current densities. (d) Cyclic stability after 5k charge-discharge cycles at 5 A g^{-1} .

Two-electrode asymmetric devices were assembled from an activated carbon (AC) used as negative electrode and $\text{MnO}_2\text{eMXene}$ composite (MeM) as positive electrode. Mass loadings were balanced based on capacitance values calculated from galvanostatic charge-discharge measurements at the same current density in corresponding electrolytes. They were tested in KOH as well as Na_2SO_4 electrolytes. From CV as well as from galvanostatic measurements (Figs. 7a and 7b), the AC//MeM device was operated in a greater voltage window of 2.0 V in Na_2SO_4 electrolyte (AC//MeM- Na)⁵⁴ while it was limited to 1.6 V in KOH (AC//MeM-K). In contrast, the capacitance of the device (relative to the mass of both electrodes) is lower in Na_2SO_4 electrolyte (35 F g^{-1}) than in KOH (47 F g^{-1}) and the difference is obviously assigned to the greater capacitance of the $\text{MnO}_2\text{eMXene}$ positive electrode in the latter electrolyte (Fig. 5a and 6a: 272 F g^{-1} in KOH versus 165 F g^{-1} than in Na_2SO_4). This balance of both device capacitance and voltage leads to energy densities in the same range (Fig. 7c). These were calculated from galvanostatic

charge-discharge data. The AC//MeM-Na device shows an energy density of 19.3 Wh kg⁻¹ at 500 W kg⁻¹, while the value decreased to 4.4 Wh kg⁻¹ at 10k W kg⁻¹. AC//MeM-K device presents 11 Wh kg⁻¹ energy density at 8k W kg⁻¹, although it showed 16.8 Wh kg⁻¹ at 400 W kg⁻¹, revealing an attractive energy-density retention at high power. The cycling stability was also evaluated for both devices (Fig. 7d). After 10k charge-discharge cycles, capacitances of both devices operated in KOH and Na₂SO₄ electrolytes decreased to about 77% of their initial capacitance. Most of the losses occurred during the first 2k cycles. To assign the origin of these fadings, Ohmic drop as well as Coulombic and energy efficiencies were analyzed (Fig. S3). In KOH electrolyte, the apparent decrease of specific capacitance during the first 2000 cycles can be assigned to the observed evident reduction of the energy efficiency. Then, the device suffered a gradual capacitive decay in extra cycles. On the other hand, there are also a visible fading of the energy efficiency over initial 1000 cycles when the device was operated in Na₂SO₄ electrolyte, though the capacitance fading is more limited. Additionally, it exhibits slight increase of Ohmic drop over cycles in both applied electrolytes.

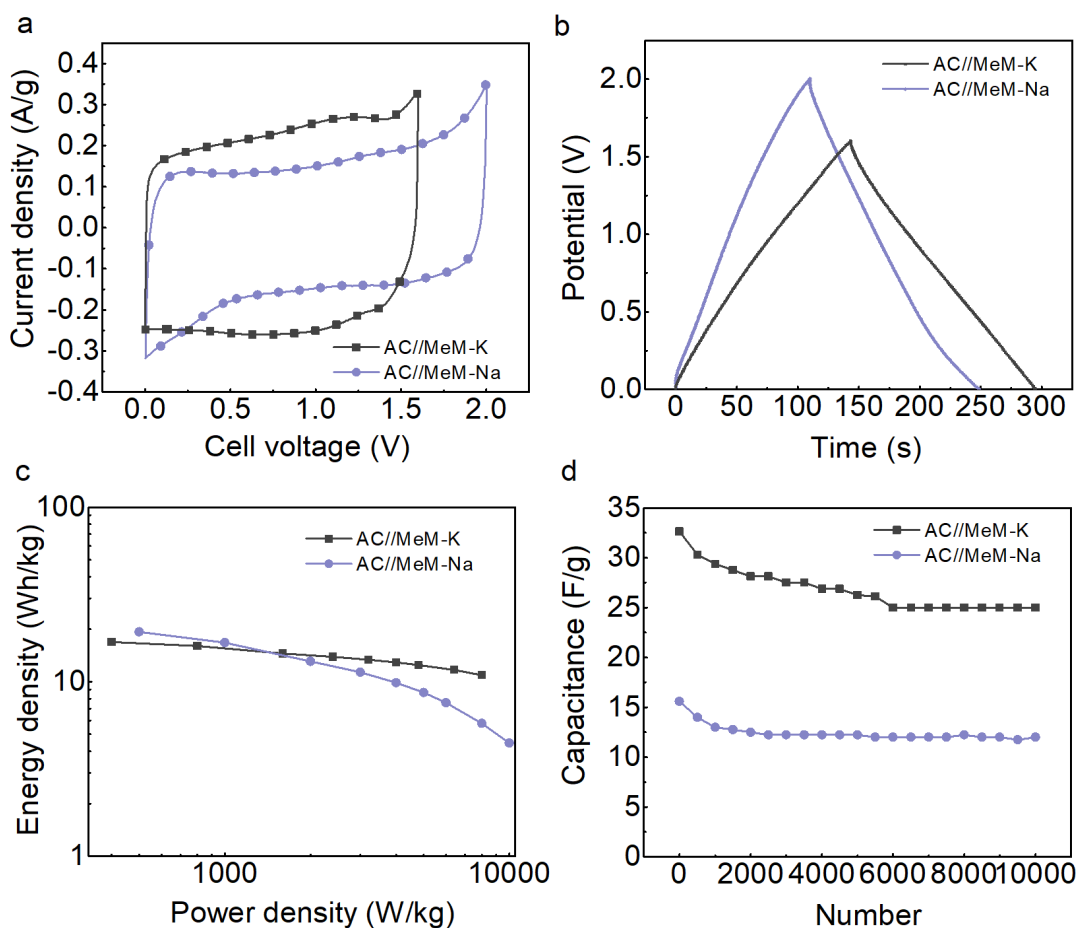


Figure 7. The electrochemical performance of AC//MeM-K and AC//MeM-Na devices in neutral (Na₂SO₄ 1 M) and alkaline electrolytes (KOH 1 M). (a) Cyclic voltammogram test at 20 mV s⁻¹. (b) galvanostatic charge discharge curve at 0,5 A g⁻¹. (c) Ragone plots for the full cell. Power and energy densities are normalized by the mass of both electrodes. (d) Cycling Longevity in 10k charge-discharge cycles.

CONCLUSION

Two different MnO_2 polymorphs and their mixtures were synthesized by adjusting the temperature of the co-precipitation reaction. According to XRD patterns and SEM images, below $80\text{ }^\circ\text{C}$, $\delta\text{-MnO}_2$ was obtained while $\alpha\text{-MnO}_2$ was prepared at greater temperatures. This structural change was evidenced as the powder morphology evolved from $\delta\text{-MnO}_2$ nano-sheets to $\alpha\text{-MnO}_2$ nano-fibers. Moreover, $\text{MnO}_2\text{-120}$ sample prepared at $120\text{ }^\circ\text{C}$ appeared as a mixture of δ and α phases with nano-sheets and fibers. As an electrode in a three-electrode setup, $\text{MnO}_2\text{-120}$ electrode not only exhibited a high capacitance (196 F g^{-1} at 0.5 A g^{-1}) just like $\delta\text{-MnO}_2$, but also held the rate performance of $\alpha\text{-MnO}_2$. Exfoliated Ti_3C_2 MXene layers with negative surface charges were introduced in the co-precipitation medium, allowing Mn^{2+} cations to adsorb while reacting at $120\text{ }^\circ\text{C}$ with Mn^{7+} to give MnO_2 sand-roses particles grown at the MXene layer surface. The resulting composite was characterized by X-ray powder diffraction and electron microscope measurements. An $\text{MnO}_2\text{eMXene}$ -based electrode was initially studied in a three-electrode cell, using KOH and Na_2SO_4 electrolytes. In KOH it delivered a capacitance performance of 272 F g^{-1} at 0.5 A g^{-1} and kept 93% of capacitance retention over 5k charge-discharge cycles at a current density as high as 5 A g^{-1} . On the other hand, in Na_2SO_4 electrolyte, $\text{MnO}_2\text{eMXene}$ electrode showed a 165 F g^{-1} capacitance at 0.5 A g^{-1} and 81 F g^{-1} at 10 A g^{-1} , implying a 50% of rate capability in this current range. From 106 F g^{-1} , any capacitance fading could be observed over 5k charge-discharge cycles at 5 A g^{-1} current density. In a second step, asymmetric devices built on $\text{MnO}_2\text{eMXene}$ (MeM) and commercial activated carbon in both electrolytes were fabricated and evaluated. Compared with the AC//MeM-K operated in KOH owning a 1.6 V working voltage window, AC//MeM-Na device takes benefit from a larger potential window of 2 V in Na_2SO_4 , confirming the advantages of neutral electrolytes. As such, AC//MeM-Na displayed a 19.3 Wh kg^{-1} (500 W kg^{-1} power density) energy density while it was 16.8 Wh kg^{-1} at 400 W kg^{-1} for AC//MeM-K. In contrast, AC//MeM-Na showed a drastic energy-density fading at 4.4 Wh kg^{-1} at 10 KW kg^{-1} , while AC//MeM-K device kept a remarkable energy density of 11 Wh kg^{-1} at a 8 KW kg^{-1} power density.

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