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Stable high-voltage aqueous pseudocapacitive energy storage device with slow self-discharge

Hemesh Avireddy^a, Bryan W. Byles^{c,d}, David Pinto^{c,d}, Jose Miguel Delgado Galindo^a, Jordi Jacas Biendicho^a, Xuehang Wang^{c,d}, Cristina Flox^a, Olivier Crosnier^{e,f}, Thierry Brousse^{e,f}, Ekaterina Pomerantseva^{c,d}, Joan Ramon Morante^{a,b}, Yury Gogotsi^{c,d,*}

^aIREC, Catalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 08930, Sant Adria de Besos, Spain

^bFaculty of Physics, University of Barcelona, Barcelona, Spain

^cDepartment of Materials Science & Engineering, Drexel University, Philadelphia, PA, 19104, USA

^dA.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA, 19104, USA

^eInstitut des Materiaux Jean Rouxel (IMN), CNRS UMR 6502-Universite de Nantes, 2 rue de la Houssiniere BP32229, 44322, Nantes Cedex 3, France

^fReseau sur le Stockage Electrochimique de l'Energie, FR CNRS 3459, 80039, Amiens Cedex, France

* Corresponding author. Department of Materials Science & Engineering, Drexel University, Philadelphia, PA, 19104, USA.

E-mail address: yg36@drexel.edu (Y. Gogotsi).

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Abstract

We demonstrate an asymmetric supercapacitor in a potassium acetate-based water-in-salt electrolyte, where 2-D titanium carbide MXene and manganese oxide were used as negative and positive electrode materials, respectively. Use of water-in-salt electrolyte enables the assembled asymmetric device to be operated up to a cell voltage of 2.2 V, which overcomes the limited cell voltage issue in aqueous pseudocapacitors (1.2 - 1.4 V). This cell shows excellent rate capability (~48%) between 5 and 100 mV s⁻¹ and good stability (~93%) throughout 10,000 charge-discharge cycles (at 1 A g⁻¹) and 25 h voltage-hold at 2.2 V, which is competitive when compared with the performance of known asymmetric supercapacitors designed with activated carbon electrodes and fluorinated-imide based water-in-salt electrolytes. Moreover, our device shows slower self-discharge and ~32% higher volumetric energy density than activated carbon-based supercapacitors and is promising for applications where volumetric energy density is critical.

1. Introduction

Pseudocapacitive materials store electric charge by fast redox reactions [1,2]. Cyclic voltammetry profiles of this charge storage mechanism are similar to those of double-layer capacitors [1,3–5]. Furthermore, as most pseudocapacitive materials have high specific weight, the electrode made of these materials often display packing densities greater than 1 g cm⁻³. Both factors, contributes to a higher volumetric capacitance (> 50 F cm⁻³ [6,7]) than porous carbon-based electrodes (15–25 F cm⁻³ [2,8]). Therefore, pseudocapacitive materials are more promising than porous carbons, specifically in applications where the size or volume of the device is critical [8]. RuO₂ [9,10], IrO₂ [11], H_{3+x}IrO₄ [12], MnO₂ polymorphs [13], V₂O₅ [14], Fe₃O₄ [15], FeWO₄ [16], Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} [17], MnFe₂O₄ [18], ZnMn₂O₄ [19], La_{1-x}Sr_xMnO₃ [11] are examples of oxides which store charge via pseudocapacitive behavior. Most of these oxides exhibit superior capacitance values in aqueous electrolytes, but since the electrochemical potential of water-splitting reaction is low in aqueous electrolytes, supercapacitors fabricated with these materials operate within a restricted voltage window (less than 1.23 V) [20]. The narrow cell voltage results in a limited energy density for devices operated in aqueousbased electrolytes since the energy in a supercapacitor is proportional to the square of the cell voltage, as shown by Eq. (1):

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

where E is the energy (J), C is the capacitance (F) and V is the cell voltage (V).

The use of super-concentrated solutions, such as water-in-salt electrolytes, is a promising approach to increase cell voltage and thus address the issue of limited energy densities of aqueous-based capacitors. In water-in-salt electrolytes, the amount of salt is greater than water (mass_{salt}/mass_{water} or volume_{salt}/volume_{water} > 1) [21,22], which reduces the kinetics of water splitting reactions and allows for widening of the cell voltage window [22]. For

instance, the use of 21m(mol kg⁻¹) lithium bis(trifluoromethane)-sulfonimide (LiTFSI) enables the extension of the electrochemical potential window of MnO₂ up to 1.4 V, which was previously limited to 1.0 V in standard aqueous electrolytes [23]. However, the fade of capacitance with the increase of scan rate was higher in 21m LiTFSI (< 20%) compared to standard aqueous electrolytes (> 45%, 5M LiNO₃) [23]. For MnO₂ electrode, such a fast decay was attributed to lower ionic conductivity of 21m LiTFSI (< 10 mS cm⁻¹) over standard aqueous electrolytes (> 50 mS cm⁻¹) [23], which was related to the strong electrostatic interaction between cation's and anion's in 21m LiTFSI. Recently, it was found that due to the weak Lewis acidity of potassium ions, or weak interaction of acetate anion's [24,25], potassium acetate-based water-in-salt electrolytes exhibits higher ionic conductivities (> 20 mS cm⁻¹) than LiTFSI based water-in-salt electrolytes (< 10 mS cm⁻¹) [24,26]. Also, an electrolyte concentration of 21m potassium acetate represents a reduction of water molecules in the solvation shell of potassium ions, as demonstrated previously by Tian et al. by Raman characterization [27]. Therefore, the use of 21m potassium acetate as a water-in-salt electrolyte appears to enhance the rate capability of asymmetric pseudocapacitors.

Beyond using a concentrated electrolyte, the use of suitable electrode material is required for achieving high rate capability in supercapacitors. So far, only MnO₂ has been reported to show pseudocapacitance in water-in-salt electrolytes [23,28]. The properties of charge storage in MnO₂ vary significantly between polymorphs as well as with the type of electrolyte used [29]. There are many polymorphs of MnO₂ whose crystal structures differ in the arrangement of MnO₆ octahedra, including tunnel and layered crystal structures [13,26]. Birnessite, Spinel, Ramsdellite, Todorokite, Cryptomelane, Pyrolusite and OMS-5 are some known polymorphs of MnO₂. Among these, Cryptomelane (α -MnO₂) can show high rates, as it exhibits a higher electronic conductivity (9 mS cm⁻¹) than other polymorphs (< 3 mS cm⁻¹ [13,26]). However, due to the formation of soluble species (Mn²⁺) within the negative potentials (vs. Ag/AgCl) [29], MnO₂ is limited to the positive potential windows. Therefore, it is important to find a material which shows pseudocapacitive behavior under negative potentials, which would allow designing an asymmetric supercapacitor with an expanded voltage window [30–34]. Considering this, a 2-D MXene such as titanium carbide (Ti₃C₂) is a promising electrode material to pair with MnO₂, as it demonstrates high electronic conductivity (> 5,000 S cm⁻¹) and exhibits high volumetric capacitance in a negative electrochemical windows vs. Ag/AgCl (~1500 F cm⁻³) [35–37]. According to Shpigel et al. [38] and Sugahara et al. [39], the capacitive-like charge storage is due to the intercalation of hydrated cation ions within the interlayer spacing of Ti₃C₂ MXene, and Kim et al. [40] has reported that the use of highly concentrated electrolytes such as hydrate melt of Li (TFSI)_{0.7}(BETI)_{0.3}·2H₂O allows the dense accumulation of hydrated cations in the MXene interlayers enhancing the values of capacitance. Taking account of these properties, the use of Ti₃C₂ MXene as a negative electrode coupled with a positive MnO₂ electrode in a concentrated potassium acetate-based water-in-salt electrolyte can enable an asymmetric supercapacitor. Given this motivation, herein we demonstrate a 2.2 V high-voltage asymmetric supercapacitor in a 21m of potassium acetate-based water-in-salt electrolyte, where Ti₃C₂ MXene and α -MnO₂ are implemented as negative and positive electrodes, respectively. We discuss the electrochemical performance of this device in terms of rate capability, long-term cycling stability and self-discharge and compare its cycling stability with the recently reported hybrid cell using water-in-salt electrolytes.

2. Materials and methods

2.1. Synthesis of α -MnO₂

α -MnO₂ nanowires were prepared as previously described [40]. 316 mg of potassium permanganate (KMnO₄, 99+%, Acros Organics) and 108 mg of ammonium chloride (NH₄Cl, 99.5%, Strem Chemicals) were dissolved in 100 mL of deionized water, and 20 mL of this solution was added to a 23 mL Teflon-lined stainless steel autoclave (Parr Instrument Company). The autoclave was placed in an oven at 150 °C for 48 h, after which the product (α -MnO₂) was filtered, washed, and dried at 100 °C for 12 h.

2.2. Synthesis of Ti₃C₂ MXene

2-D Ti₃C₂ MXene was synthesized using a minimally intensive layer delamination method (MILD) [37]. 1 g of MAX phase powder of titanium aluminum carbide MAX (Ti₃AlC₂, Carbon Ukraine, particle size < 40 μ m) was added

slowly to a mixture of 1 g of lithium fluoride (LiF, 98.5% grade, Alfa Aesar) in 20 ml of 9M hydrochloric acid (HCl, 37 wt%, Alfa Aesar) to chemically etch the aluminum from the MAX phase. The reaction was stirred with a Teflon-bar for 24 h at 35°C. The products were transferred to a 50 mL centrifugation tube and washed with deionized water by centrifugation at 3500 rpm (5 min per cycle) until the pH of the dark-green supernatant was >5.5. The change in color indicates the beginning of delamination. After gathering the supernatant, settled and swollen sediment at the bottom of the centrifuge tube was collected and dispersed in deionized water (by shaking). Resulting black slurry was vacuum-filtered on a Celgard membrane 3501 (Celgard®) to form free-standing films which were dried in a vacuum oven at 120 °C overnight and then stored in a vacuum desiccator for further use.

2.3. Microstructural characterization

The morphology of MnO₂ and Ti₃C₂ films were characterized by scanning electron microscopy (SEM) using a Zeiss Supra 50VP (Germany) equipped with an Oxford Instruments energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) was carried out on a Rigaku Smartlab (Tokyo, Japan, 40 kV, and 30 mA) and a Rigaku MiniFlex (Tokyo, Japan, 40 kV and 15 mA) diffractometer using Cu K α .

2.4. Electrolyte preparation and measurements of the conductivity

Stoichiometric amount of anhydrous potassium acetate salt (CH₃COOK, 99+%, Sigma-Aldrich) and of lithium bis (Trifluoromethane)-Sulfonimide (LiTFSI, 99+%, Sigma Aldrich) were dissolved in Ar-bubbled deionized water via magnetic stirring until a homogeneous solution was obtained. Prior to the electrochemical studies, the electrolyte solution was deaerated by Ar purging. The ionic conductivity of electrolyte solutions was measured using the potentiostatic mode of electrochemical impedance spectroscopy (PEIS) at 22 °C using a two-electrode Swagelok cell. The Swagelok cell consists of a polytetrafluoroethylene body and two stainless pistons (grade 304). The measurements were done using a VMP-3 potentiostat-galvanostat (Bio-Logic, France). Frequencies applied for the measurements were taken from 1 MHz to 50 mHz, whereas an amplitude of ± 10 mV was used as applied potential. The ionic conductivity, κ (mS cm⁻¹), is calculated as:

$$\kappa = \left(\frac{1}{R_i} \right) \cdot k_c, \quad (2)$$

where, k_c is the constant, whose value is between 0.95 (max.) to 0.73 (min.). An aqueous 0.1M KCl solution was used as a standard. The ionic resistance, R_i (m Ω cm) is taken from the intercept of the real part of impedance in the Nyquist plot. Ionic conductivity was also measured for 21m of Lithium bis(Trifluoromethane)-Sulfonimide and later compared with values of 21m potassium acetate solution. The resistivity of Ti₃C₂ MXene and α -MnO₂ was evaluated by four-point measurements using a probe station (ResTest v1, Jandel Engineering Ltd., Bedfordshire, U.K.). Resistivity values were averaged with 3 measurements.

2.5. Electrochemical characterization

Measurements were carried out using a VMP-3 potentiostat/galvanostat (Bio-Logic, France), in a T-shape Swagelok cell. The cell body was made up of polytetrafluoroethylene. Polished glassy carbon was used as the current collector(s) (CHI Instruments). This cell body was used as a three-electrode configuration. Capacitance, C (F) is calculated as:

$$C = \frac{1}{v \cdot V} \int_{V_-}^{V_+} I(V) dV, \quad (3)$$

where, V (V) is the potential and v (mV s^{-1}), the scan rate. V_+ and V_- is the value of vertex potential in the positive and negative electrochemical window. I (mA) is the current response to the applied voltage, in the cyclic voltammetry technique. The capacity (mAh) is calculated as:

$$\text{Capacity} = \frac{C \cdot V}{3.6} \quad (4)$$

Specific capacitance (F g^{-1} or F cm^{-3}) or capacity (mAh g^{-1} or mAh cm^{-3}) was calculated by dividing Eq. (3) or (4), respectively, either by mass (g) or geometrical volume (cm^3) of the electrode. For the full cell, geometrical volume or weight of both electrodes was considered. The thickness of the membrane was not taken into account while measuring the volumetric performance. The Energy, E (in J) is calculated using Eq. (1). The Energy in mWh is calculated by dividing Eq. (1) by 3.6. The power, P (in mW) is calculated as:

$$P = \frac{E \cdot v}{V}, \quad (6)$$

where, E (J) is the energy of the cell, v (Vs^{-1}) is the scan rate of the CV and V (V) is the cell voltage. Energy and power density was calculated by dividing Eq. (1) or (6), respectively, either by mass (g) or geometrical volume (cm^3) of both electrodes.

2.5.1. Three-electrode cell measurements

For three-electrode cell measurements, an over-capacitive electrode made of activated carbon (YP50) was used as a counter electrode (YP50: PTFE – wt. ratio 95:5, >5 times the weight of the working electrode), a saturated calomel electrode as a reference (SCE, CHI Instruments), and Celgard membrane 3501 as the separator (Celgard®, >4mm diameter). Polished glassy carbon was used as the current collector(s) (CHI Instruments). MnO_2 , as an active material, was mixed with a conductive carbon additive (AB, Acetylene Black, Alfa Aesar) and binder (polytetrafluoroethylene, PTFE; Sigma Aldrich) in the mass ratio of 75:20:5, respectively. The powders were mixed with a low volume of ethanol and the resulting slurry was heated up to 60°C while being magnetically stirred to evaporate the solvent. Finally, the paste was rolled to form a homogenous film. The thickness, weight loading and packing density of MnO_2 films were $\sim 100 \mu\text{m}$, $\sim 12.5 \text{ mg cm}^{-2}$ and $\sim 1.28 \text{ g cm}^{-3}$, respectively, and of Ti_3C_2 films were $\sim 8 \mu\text{m}$, $\sim 2.2 \text{ mg cm}^{-2}$ and $\sim 2.75 \text{ g cm}^{-3}$, respectively. Both MnO_2 and Ti_3C_2 films were punched into a circular disk shape of 3mm in diameter and used as working electrodes. The weight of the electrodes was determined using PerkinElmer AD-6 microbalance.

2.5.2. Assembly and electrochemical characterization of the cells

Measurements were carried out using in a Swagelok cell. The cell body was made up of polytetrafluoroethylene. Polished glassy carbon was used as the current collector(s) (CHI Instruments). For comparison of the electrochemical properties of the $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ asymmetric supercapacitor, an asymmetric cell of activated carbon (YP-50//YP-50) was assembled using YP-50, Acetylene Black and PTFE in the mass ratio of 75:20:5, respectively. The thickness, weight loading and packing density of YP-50 film were $\sim 50 \mu\text{m}$, $\sim 4.5 \text{ mg cm}^{-2}$ and $\sim 0.9 \text{ g cm}^{-3}$, respectively. A mass balancing approach was carried out to equilibrate the charges between the positive and negative electrode [41,42] by:

$$R = \left(\frac{m_+}{m_-} \right) = \left(\frac{C_- \Delta V_-}{C_+ \Delta V_+} \right), \quad (5)$$

where m_+ and m_- represent the mass, C_+ and C_- the capacitance, and ΔV_+ and ΔV_- the potential window of the positive and negative electrode. The R-value, from Eq. (5), between the positive and negative carbon electrodes, was ~ 1.3 . For comparative purpose, dimensions of the MnO_2 electrode were also adjusted nearly to the thickness and diameter of YP-50 electrodes; with a weight loading of $\sim 9 \text{ mg cm}^{-2}$ and a density of $\sim 1.6 \text{ g cm}^{-3}$ ($\sim 55 \mu\text{m}$ thick). Ti_3C_2 films were also adjusted to a thickness of $\sim 10 \mu\text{m}$ ($\sim 3.0 \text{ g cm}^{-2}$, $\sim 3.0 \text{ g cm}^{-3}$). The average mass ratio, R-value, between $\alpha\text{-MnO}_2$ and Ti_3C_2 was ~ 3.6 . Prior to cell assembly, both $\alpha\text{-MnO}_2$ (positive) and Ti_3C_2 (negative) electrodes were pre-cycled in a three-electrode configuration at a scan rate of 5 mV s^{-1} for 5 cycles and then polarised to -0.2 V vs. SCE. After the assembly of the precycled electrodes in a $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ cell configuration, consecutive voltage-

hold tests were implemented to determine the operational cell voltage. To do so, the cell was held at different voltages for a duration of 2 h during which the leakage current was measured. Upper cut-off voltage was determined by the electrochemical potentials of water splitting on glassy carbon (current collector). Impedance behavior of the $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cell was measured in the potentiostatic mode of electrochemical impedance spectroscopy (PEIS) technique at frequencies from 200 kHz to 10 mHz. The amplitude of the applied potential was ± 10 mV. Fits to impedance data using an equivalent circuit were conducted using Zview software.

2.5.3. Self-discharge measurements

Self-discharge in $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ and YP-50//YP-50 cells was evaluated by measuring the open circuit voltage of cells after being charged to their optimum voltage at a current density of 10 mA g^{-1} , holding cell voltage for 2 h and then releasing the voltage. For self-discharge investigation of Ti_3C_2 and $\alpha\text{-MnO}_2$ electrodes in the asymmetric cell $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ configuration was carried out with the reference incorporated T-shape Swagelok cells. The asymmetric cell of $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ was held at 2.2 V for a duration of 25 h. Electrochemical potentials of the Ti_3C_2 and $\alpha\text{-MnO}_2$ electrodes were determined with reference to SCE.

2.5.4. Electrochemical stability measurements

Stability of the asymmetric $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cell was analyzed by using galvanostatic mode of charge-discharge at a current density of 1 A g^{-1} over 10,000 cycles. The applied current density was normalized by the mass of both electrodes. Voltage hold tests were performed for 25 h at the maximum cell voltage (2.2 V) and the response of the leakage current was observed.

3. Results and discussions

2-D Ti_3C_2 MXene is prepared via the MILD method by etching the layered Ti_3AlC_2 MAX [37], see methods for details. XRD patterns of Ti_3AlC_2 MAX and Ti_3C_2 MXene are shown in Fig. S1 (ESI). The disappearing of MAX peaks (noticeably, (104)) to the benefit of (00l) peaks of the MXene agrees with previous reports [37] and demonstrates efficient leaching of Al from the Ti_3AlC_2 MAX precursor and its conversion into Ti_3C_2 MXene. EDS analysis also confirms the absence of Al on the Ti_3C_2 MXene film, (Fig. S2b). The transition from a 3-D MAX micrometric particles to a film of MXene made of 2-D nano-flakes induces diffraction peak broadening and, in particular, a shift of (002) peak from 9.48° to 7.16° (2θ) (Fig. 1a). The shift of (002) peak in XRD pattern agrees with the restacked film structure observed in the SEM image (Fig. 1b) and indicates an increase of d-spacing from 9.31 \AA to 12.38 \AA for the Ti_3C_2 MXene phase. This is in agreement with the presence of water molecules between the interlayers of MXene [37].

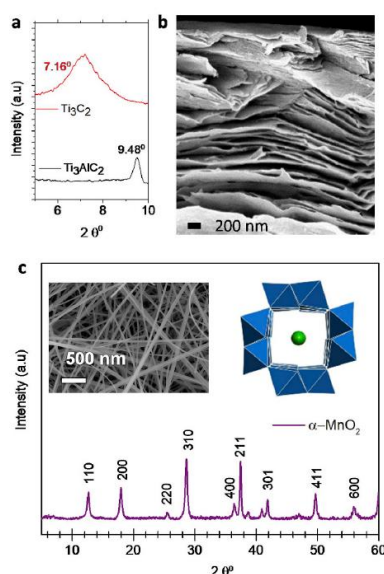


Fig. 1.

(a) XRD pattern of Ti_3AlC_2 MAX and Ti_3C_2 MXene focused on $5\text{--}10^\circ$ (2θ) (002) region (extended XRD pattern available in Fig. S1, ESI).

(b) SEM image of a Ti_3C_2 MXene film after etching, showing layered film morphology (stacked flakes of MXene).

(c) XRD pattern of $\alpha\text{-MnO}_2$. Inset, left: SEM Image of $\alpha\text{-MnO}_2$, right: Schematic of $\alpha\text{-MnO}_2$ structure (green circle represents intercalated K^+ ions and MnO_2 octahedra are represented in blue).

EDS analysis on the Ti_3C_2 MXene film indicates the presence of F, Cl and O elements, which could be in the form of surface terminal groups with Ti_3C_2 MXene (Fig. S2b).

It is noteworthy that the d-spacing of 12.38 Å in the MXene film is a relatively large interlayer space, which is feasible for the intercalation of either K^+ ions [43] (ionic radii of K^+ ion = 1.37 Å [44]) or solvated $\text{K}(\text{H}_2\text{O})_{7-x}^+$ (~1.37 - 2.80 Å [44]). The measured resistivity of the Ti_3C_2 MXene film using four probe was 0.541 ± 0.014 mΩcm (See methods), which is in good agreement with the reported values (0.56–0.46 mΩcm [45]).

$\alpha\text{-MnO}_2$ was prepared via hydrothermal method [40]. SEM image shows the morphology of nanowire (Fig. 1c, inset), which is expected to be beneficial for the electrochemical applications as demonstrated in Ref. [46]. The XRD pattern of $\alpha\text{-MnO}_2$, as shown in Fig. 1c, is indexed to tetragonal I4/m phase (JCPDS card # 44-014), which indicates the presence of 1×1 and 2×2 tunnel with an aspect of ~7.0×7.0 Å and ~2.3×2.3 Å, respectively. Besides, non-existence of intense peaks below 12° (2θ) suggests the absence of a tunnel side larger than two octahedra [46]. A schematic of the tunnel size consisting of two octahedra is shown in Fig. 1c, inset. Notably, the maximal ion radius to be able to access the 2×2 tunnel structure is 1.30 Å, as calculated based on the distance between oxygen-oxygen atoms in tunnel site [29]. This maximal ion radius of $\alpha\text{-MnO}_2$ being closer to the ionic radii of K^+ ion (1.37 Å [44]), which indicates the possibility of intercalation of K^+ ions in $\alpha\text{-MnO}_2$. EDS analysis on the $\alpha\text{-MnO}_2$ samples indicate the presence of K element (Fig. S2c, ESI), which is in agreement with the previous reports [47]. The presence of these stabilizing ions provides an efficient diffusion of the electrolyte ions into the tunnel structure during the charging/discharging process [46,47]. The measured resistivity of $\alpha\text{-MnO}_2$ pellets was 295.67 ± 13.3 Ωcm.

In order to highlight the importance of using the water-in-salt electrolyte over conventional aqueous electrolytes, the electrochemical properties of Ti_3C_2 MXene were measured in a conventional 1m and 21m potassium acetate based water-in-salt based electrolyte using the cyclic voltammetry (CV) technique in a three-electrode cell configuration. The CV curve of Ti_3C_2 MXene in 1m at a scan rate of 5 mVs⁻¹ shows a capacitive-like profile (Fig. S3a, ESI; CV curves of glassy carbon current collector are shown in Fig. S3b, ESI) with a gravimetric capacity of 21.9 mAhg⁻¹ (79 Fg⁻¹). The CV curve also indicates that the negative vertex potential for Ti_3C_2 MXene electrode in 1m was -1.1 V vs SCE (Potential window: -0.1 V to -1.1 V vs. SCE) which shifts to -1.6 V vs SCE when Ti_3C_2 MXene was examined in 21m potassium acetate water-in-salt electrolyte (Potential window: -0.1 V to -1.6 V vs. SCE). This extension of vertex potential with the transition from the conventional to water-in-salt electrolytes is consistent with the recent findings of Tian et al. [27] on the electrochemical behavior of potassium acetate based water-in-salt electrolytes for K^+ ion batteries. Interestingly, the CV curve indicates a capacity value of 32 mAhg⁻¹ for Ti_3C_2 MXene in 21m potassium acetate based water-in-salt electrolyte, which was higher than the value obtained in conventional 1m of potassium acetate electrolyte (21.9 mAhg⁻¹, 5 mVs⁻¹). This trend is also in agreement with the recent report of Kim et al. [48] in which the rise of capacity in the highly concentrated electrolyte is attributed to the dense accumulation of hydrated cations in the MXene interlayers. Considering the advantage of both wider negative vertex potential and higher capacity for Ti_3C_2 MXene in water-in-salt electrolytes with respect to conventional 1 m, further studies were carried out using super-concentrated electrolyte. Two electrolyte concentrations were investigated: 21m and 30 m, using Ti_3C_2 MXene films as electrode. The plot of log scheme of current over scan rate shows a higher slope for 21m (0.91) than for 30m (0.79) (Fig. S4c, ESI). Since the slope of 21m is closer to 1, it represents capacitance independence over rate with a reversible behavior [43]. This enhanced reversible behavior for the 21 potassium acetate electrolyte is attributed to its higher ionic conductivity (53.6 ± 1.4 mS cm⁻¹) with respect to the conductivity of 30m potassium acetate electrolyte (27.80 ± 1 mS cm⁻¹, calculated using Eq. (2)). As a whole, the molality of 21m potassium acetate electrolyte shows better kinetic of insertion/diffusion of K^+ ions within the interlayers of Ti_3C_2 MXene so it was selected as super-concentrated electrolyte for further analysis and device assembly.

The electrochemical properties of Ti_3C_2 MXene and $\alpha\text{-MnO}_2$ were measured by CV technique and the response at a scan rate of 5 mVs⁻¹ is shown in Fig. 2. The charge storage of Ti_3C_2 MXene in 21m of potassium acetate, as calculated from the CV curve using Eq. (4), corresponds to a volumetric capacity of ~100 mAh cm⁻³. Whereas, the CV curve of $\alpha\text{-MnO}_2$ shows a pseudocapacitive performance originating from surface redox reactions [4,29]. This charge storage corresponds to a capacity of ~14 mAh cm⁻³. Electrochemical analyses also show that the negative potential limit of Ti_3C_2 MXene is close to -1.6 V vs. SCE, whereas $\alpha\text{-MnO}_2$ can be cycled up to 0.95 V vs. SCE. Convoluting the scanning electrochemical potential window (SPW) of both electrodes gives the possibility to achieve a cell voltage up to 2.55 V. CV curves of 21m of potassium acetate electrolyte on a glassy carbon indicate that the

negative and positive vertex potentials are -1.6 V and 1.1 V vs. SCE, respectively (Fig. S5, ESI), which convolutes to a maximum voltage of

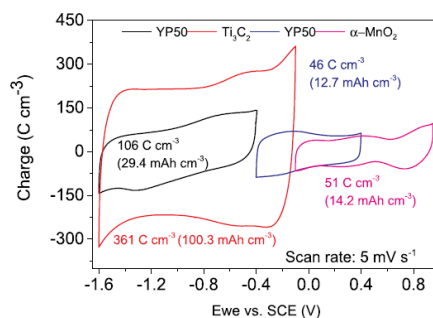


Fig. 2.

Cyclic voltammogram of Ti_3C_2 MXene films, YP50 and $\alpha\text{-MnO}_2$ ($2 \times 2 \text{ MnO}_2$) individual electrodes in a three-electrode configuration following the potential windows of their respective device (black and blue traces for YP-50//YP-50 and, red and purple traces for Ti_3C_2 // $\alpha\text{-MnO}_2$), at scan rate of 5 mV s^{-1} in 21m potassium acetate electrolyte.

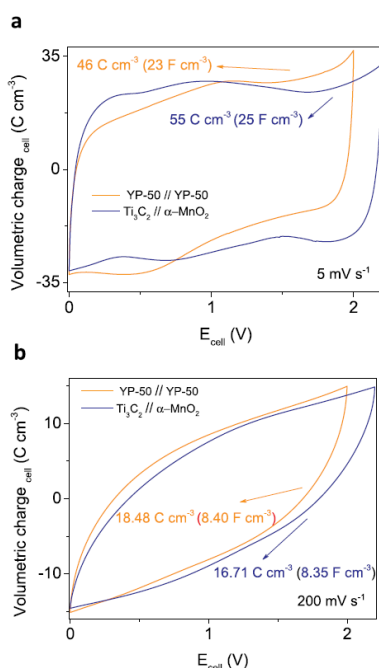


Fig. 3. Cyclic voltammograms of the YP-50//YP-50 and Ti_3C_2 // $\alpha\text{-MnO}_2$ cells (orange and blue trace, respectively) at (a) low rate (5 mV s^{-1}) and (b) high rate (200 mV s^{-1}) in 21m potassium acetate electrolyte.

2.7 V. However, Voltage-hold tests convey to a different value for the maximum cell voltage. Beyond 2.2 V, the value of leakage current is unstable during the voltage-hold tests (Fig. S6, ESI) which implies cell failure. This failure is caused by the widening of the potential window of $\alpha\text{-MnO}_2$ in order to respond the increase of cell voltage (Fig. S7 and Fig. S8, ESI), which leads to the formation of soluble Mn^{2+} species [29]. Considering these analyses, the asymmetric cell of Ti_3C_2 // $\alpha\text{-MnO}_2$ was operated between 0 to 2.2 V. The CV curve at a scan rate of 5 mV s^{-1} , as shown by Fig. 3a, demonstrates that the Ti_3C_2 // $\alpha\text{-MnO}_2$ cell shows a rectangular shape profile which is typical of capacitive-like charge storage. The galvanostatic charge and discharge curves measured at a current density of 0.25 A g^{-1} (Fig. S9, ESI) show a linear voltage-time response, which also indicates a capacitive behavior of the Ti_3C_2 // $\alpha\text{-MnO}_2$ cell.

The Nyquist plot of Ti_3C_2 // $\alpha\text{-MnO}_2$ cell and equivalent circuit used for data fitting are shown in Fig. S10 (ESI). Impedance data show a high frequency semicircle with an inclined spike of $\sim 45^\circ$ at intermediate frequencies (Fig. S10a, ESI), which terminates in an open circuit or capacitive behavior at even lower frequencies (Fig. S10b, ESI). Impedance data was fitted using a modified version of the Randles circuit (Fig. S10c, ESI), in which the typical double layer capacity (Cdl) has been substituted by a CPE_1 in order to fit the non-ideal high frequency semicircle. Other circuit elements, such as the R_1 , R_2 and Z_w can be correlated to electrolyte resistance, charge-transfer resistance and ionic diffusion across the electrode-electrolyte interface, respectively. This impedance behavior is characteristic of a pseudocapacitor system as previously by Kurra et al. with asymmetric cell of Ti_3C_2 MXene// RuO_2 pseudocapacitors [49]. Besides this, Nyquist plots measured between 1.4 to 2.2 V show a phase angle close to that of 70° at a

frequency of 10 mHz (Fig. S10d, ESI), which also illustrates a pseudocapacitive type charge storage behavior as previously demonstrated by Levi et al. in Ti_3C_2 MXene using an aqueous electrolyte [43].

For comparison with a non-pseudocapacitive cell, an asymmetric supercapacitor based on activated carbon electrodes (YP-50) was also assembled, hereafter referred as YP-50//YP-50 (see methods). The CV curves at 5 mV s^{-1} for both, YP-50//YP-50 and $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cell are shown in Fig. 3a. The response of $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cell corresponds to a capacitance of 25 F cm^{-3} (or capacity of $\sim 15 \text{ mAh cm}^{-3}$), which is close to that of YP-50//YP-50 cell, 23 F cm^{-3} (or capacity of $\sim 13 \text{ mAh cm}^{-3}$, as calculated based on Eqs. (3) and (4)). CV curves at 200 mV s^{-1} in Fig. 3b show resistive behavior for both YP-50//YP-50 and $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cells and the rate decay at $C_{5\text{mV s}^{-1}}/C_{100 \text{ mV s}^{-1}}$ (Fig. S11, ESI), which measures a value of the capacitance over the scan rate, indicates a similar value ($\sim 48\%$) for both the asymmetric YP-50//YP-50 and $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cells. Comparing these results with the literature, capacitance fade of the asymmetric $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ supercapacitor is lower than the existing carbon-MnO₂ hybrid capacitor operated using 21m LiTFSI water-in-salt electrolyte ($\sim 17.6\%$) [23]. The resulting low capacitance decay for the asymmetric supercapacitor is credited to the higher ionic conductivity of 21m potassium acetate ($53.6 \pm 1.4 \text{ mS cm}^{-1}$) over 21m LiTFSI water-in-salt electrolyte ($7.14 \pm 0.18 \text{ mS cm}^{-1}$, as calculated based on Eq. (2)).

In addition to this, self-discharge measurements were conducted for YP-50//YP-50 and $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cells and results are presented in Fig. 4. In Fig. 4a–f, both cells were charged at different voltages (from 1.5 V to 2.0 V) for 2 h and the percentage of final to initial voltage ($V_0 - 1$) was plotted as a function of time or log time. Measurements as a function of time for $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ and YP-50//YP-50 in Fig. 4 a and b, respectively, indicate better voltage retention for the asymmetric $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ supercapacitor, suggesting a reduced charge-redistribution compared to YP-50//YP-50 cell. Analyses of self-discharge in log time within the initial period ($< 100 \text{ s}$), Fig. 4 c and d, show a linear drop after a plateau, whereas voltage decays linearly for the intermediate period ($> 100 \text{ s}$), Fig. 4 e and f. This behavior suggests the presence of an activation-controlled Faradaic mechanism in both cells at that time frames. The presence of an activation-controlled Faradaic process in YP-50//YP-50 cell is likely due to the oxidation/reduction of carbon functionalities, as previously observed by Black et al. [50,51]. However, an activation-controlled Faradaic process and restricted charge-redistribution behavior in the $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cell is related to its pseudocapacitive behavior, as previously reported with self-discharge analysis of the pseudocapacitive materials MnO₂ and RuO₂ by Andreas et al. [51,52].

Unlike in standard aqueous electrolytes [52], YP-50//YP-50 in water-in-salt electrolyte exhibits much higher time response (Fig. 5a). Such low self-discharge ($> \text{few mins}$) is attributed to the diffusion limitation of charges at the interface between the electrolyte and electrode (fluid-solid interface, FSI [53]), which can be emphasized by the decay of voltage with $t^{-1/2}$ [54]. The deviation from linear decay of voltage with $t^{-1/2}$ in YP-50//YP-50, Fig. 5a inset, and in $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$, Fig. 5b inset, confirms the existence of a diffusion limitation [55] which is attributed to the higher viscosity of water-in-salt ($> 10 \text{ mPa s}^{-1}$ [25]) compared to standard aqueous electrolytes ($< 2 \text{ mPa s}^{-1}$ [56]). The use

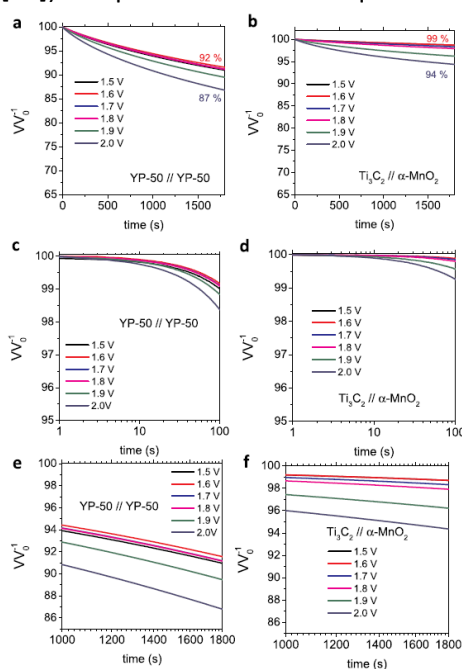


Fig. 4. Self-discharge of (a) YP-50//YP-50 and (b) $\text{Ti}_3\text{C}_2/\alpha\text{-MnO}_2$ cells at different charging voltages. The decay of the open-circuit voltage (E_{cell}) was evaluated after consecutively charging the cells from 1.5 to 2.0 V and holding E_{cell} for 2 h. The plot between voltage decay versus log in time for (c) YP-50//YP-50 and (d)

Ti₃C₂// α -MnO₂ cells and the plot between voltage decay and versus log in time for (e) YP-50//YP-50 and (f) Ti₃C₂// α -MnO₂ cells to observed the to observed the charge-redistribution and activation controlled selfdischarge reaction.

of electrolytes with high viscosities constraints the redistribution of charges at the FSI [54,55]. In the initial 30,000 s of self-discharge, the voltage of Ti₃C₂// α -MnO₂ cell fades from 2.2 V to ~1.5 V, whereas the voltage of YP-50//YP-50 reduces from 2.0 V to ~1.3 V. These decays can be quantified to ~68% and 65% of their maximum cell voltage, respectively. Interestingly, for the asymmetric supercapacitor to reach an analogous self-discharge of ~65% as in YP-50//YP-50 cell, extra 20,500 s are needed (almost 1.7 times longer) which indicates a significantly slower self-discharge.

Monitoring the electrochemical behavior of each electrode during the self-discharge of the Ti₃C₂// α -MnO₂ suggests that the voltage decay of Ti₃C₂ is initially faster, but then becomes slower after 10,000 s compared to α -MnO₂ (Fig. 5b). Diffusion limitation occurs at both electrodes, Fig. 5b inset, however voltage profiles as a function of $t^{-1/2}$ are significantly different between Ti₃C₂ and α -MnO₂ electrodes. The mechanism behind this phenomenon is still unclear and further investigations are required. However, recent experiments by Levi et al. and Ren et al. [43,57] have shown faster ion desorption from Ti₃C₂ surface sites, followed by slower desorption of trapped ions within the shallow adsorption sites of Ti₃C₂ MXene. We hypothesize that the difference of desorption rates at the surface and shallow

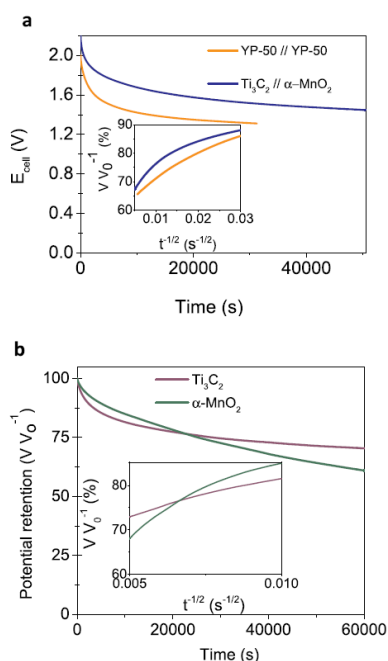


Fig. 5. (a) Self-discharge of YP-50//YP-50 and Ti₃C₂// α -MnO₂ cells. The decay of the open circuit voltage (E_{cell}) was evaluated during 8-14 h, after consecutively charging the cells to the maximum voltage 2.2 V and 2.0 V, respectively) at 10 mA g⁻¹ and holding E_{cell} max. for 2 h. (b) Potential decay of individual electrodes of the Ti₃C₂// α -MnO₂ cell measured (with respect to SCE reference electrode) after holding the maximum cell voltage for 25 h. Inset figures: The decay behaviour as the function of $t^{-1/2}$, where t represents the decay time under open circuit potential.

sites allow Ti₃C₂ MXene to show a two-step voltage decay during the self-discharge test. Whereas fast ion removal capacity test of K⁺ ions from α -MnO₂, as shown by Bylan et al. during the desalination process [46], allows the α -MnO₂ to show high voltage decay during the self-discharge analysis. As a whole, self-discharge studies suggest that different mechanisms play a role depending on the time frame. On initial and intermediate periods of time, voltage versus log time plots Fig. 4 follow the expected behavior of an activation-controlled Faradaic mechanism and, for studies conducted during long periods of time, Fig. 5, voltage profiles in square root time deviate from linearity in agreement with previous work [55] involving electrolytes with high viscosity, which indicates a diffusion-controlled self-discharge mechanism. Indeed more experiments are necessary to completely characterize the self-discharge behavior of Ti₃C₂// α -MnO₂ cell, for instance, self-discharge as float current measurements and as a function of temperature. We aim to continue this type of investigations on the Ti₃C₂// α -MnO₂ system and others in the near future.

Lastly, long-term cycling tests were performed to determine Ti₃C₂// α -MnO₂ cell stability. Long-term cycling test at a current density of 1 A g⁻¹ indicates good capacitance retention of ~93% over 10,000 cycles, Fig. 6a, with a coulombic efficiency ranging between 99.5 to 99.9% (Fig. 6a, inset). Stability analysis via voltage hold tests at 2.2 V (Fig. 6b), shows a stable leakage current and the cell is able to withstand a current response of $\sim 4 \pm 1.5$ mA g⁻¹ for 25 h. CV

curves measured before and after voltage hold tests indicate capacitance retention of 91.64% (Fig. S12, ESI). Also, these CV curves show a small voltage shift for the reductive hump, i.e. 1.83 to 1.88 V, which occurs due to the shift in

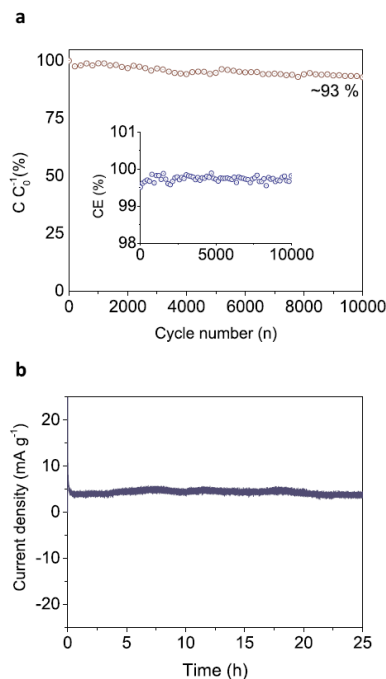


Fig. 6. Stability analysis of the $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ cell. (a) Capacitance retention, evaluated through long term galvanostatic charge discharge at 1 A g⁻¹. Inset figure: Columbic efficiency (CE) during long term cycling. (b) Observed leakage current during the hold tests for 25 h at a cell voltage of 2.2 V. Current density applied (a) and measured (b) are considered with respect to the mass of both electrodes.

the electrochemical potential window of Ti_3C_2 and $\alpha\text{-MnO}_2$ towards positive polarization (Fig. S13, ESI). These results prove that our asymmetric $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ supercapacitor has a very good electrochemical stability. Besides, capacitance retention as a function of cycles is significantly higher (~93%) than the one obtained for recently reported asymmetric supercapacitors, as summarized in Table 1. The stability features are better than the existing carbon// MnO_2 asymmetric cell based on water-in-salt electrolytes. In such systems, rapid decays occur within 5000 cycles [23,28] (< 50%, Table 1). In addition, the volumetric energy density of $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ cell (16.80 mWh cm⁻³ at 0.13Wcm⁻³) is ~32% higher than of YP-50//YP-50 cell (12.77 mWh cm⁻³ at 0.11Wcm⁻³). The Ragone plot (Fig. S14, ESI), which shows the relationship between the volumetric energy and power density, also indicates a higher volumetric energy and power densities for the $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ cell when compared to the YP-50//YP-50 cell. The observed volumetric energy density of $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ cell (16.80 mWh cm⁻³ at 137mWcm⁻³) is higher than the existing supercapacitors based on water-in-salt electrolytes, such as and AC// MnO_2 in 21m Li-TFSI [23] (10 mWh cm⁻³ at 44mWcm⁻³ mWh cm⁻³), AC//AC in 7m Li-TFSI [21] (6 mWh cm⁻³ at 49mWcm⁻³) and AC//AC cell in 31m Li-TFSI (8 mWh cm⁻³ at 57mWcm⁻³). These results are promising and support the use of asymmetric supercapacitors, such as this $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ configuration, in applications where the volumetric energy density are required.

4. Conclusions

We assembled an asymmetric cell with a potassium acetate-based water-in-salt electrolyte, where 2D titanium carbide MXene (Ti_3C_2) and manganese oxide ($\alpha\text{-MnO}_2$) were used as a negative and positive electrode, respectively. The high ionic conductivity of the selected potassium acetate water-in-salt electrolyte concentration, i.e. 21 m, enables the asymmetric cell to demonstrate less capacitance fade upon increasing scan rates (~48%) than the asymmetric supercapacitors operated in fluorinated-imide based water-in-salt electrolytes (~17.6%). Furthermore, the asymmetric cell also demonstrates an exceptional electrochemical stability (> 90%) during voltage-hold test and 10,000 cycles, when compared to existing asymmetric supercapacitors using water-in-salt electrolytes (50% or less after 5000 cycles). Due to pseudocapacitive charge storage mechanism and the use of a super concentrated electrolyte, the asymmetric $\text{Ti}_3\text{C}_2//\alpha\text{-MnO}_2$ cell shows slower self-discharge, analogous capacitance and a ~32% increase on volumetric energy density with respect to activated carbonbased supercapacitor. The asymmetric device is, therefore, promising for applications in which high

volumetric energy density (high voltage) is required. It is worth to mention that the cell assembly approach herein presented can be extended to other existing MXene phases to built new high-voltage asymmetric supercapacitors.

Competing financial interests

The authors declare no competing financial interests.

Table 1

Comparison of the stability of the pseudocapacitor presented in this work with other hybrid cells functioning with a water-in-salt electrolyte.

Cell type	Charging Mechanism	Electrolyte salt ^d	Capacitance Decay (Cycles)	Hold Tests- Leakage current (mA g ⁻¹ , cell)	Reference
C-MnO ₂ ^a	EDLC(-)/Pseudocapacitive(+)	LITFSI	~50% (5,000)	-	[23]
Li-MnO ₂ ^b	Plating-deplating(-)/Pseudocapacitive(+)	LITFSI	< 25% (5,000)	-	[28]
Ti ₃ C ₂ - α -MnO ₂ ^c	Pseudocapacitive(-)/Pseudocapacitive(+)	KAc	~96% (5,000) ~93% (10,000)	~4.0 \pm 1.5 (25 h)	Present work

^a Black pearl carbon (active material: 9.7 mg cm⁻²)/amorphous MnO₂ (active material: 2.9 mg cm⁻²).

^b Lithium (unknown weight)/MnO₂ (active material: 200 μ g cm⁻²).

^c Ti₃C₂ (loading ~3.0 g cm⁻², ~10 μ m thick, density ~3.0 g cm⁻³) and α -MnO₂ (loading ~9 mg cm⁻², density ~1.6 g cm⁻³, ~55 thick).

^d Concentration: 21 m (mol kg⁻¹); LiTFSI: lithium bis(trifluoromethane)-sulfonimide; KAc: potassium acetate.

Data availability

Data associated with this article is available from the corresponding author on reasonable request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nanoen.2019.103961>.







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	<p>Hemesh Avireddy is currently a researcher at the Catalonia Institute for Energy Research (Spain). He received his Ph.D in Nanosciences and Nanotechnology from the University of Barcelona in 2019. He has been as a visiting researcher at Institut des Matériaux Jean Rouxel-Polytech Nantes (France) and A. J. Drexel Nanomaterials Institute, Drexel University (US). His research activities are focused on the electrode assembly and architecture for the electrochemical energy storage devices.</p>
	<p>Bryan W. Byles received his bachelor's degree in Materials Science and Engineering from Rutgers University in 2013, followed by his Ph.D. from Drexel University in the Department of Materials Science and Engineering in 2018. He worked under Dr. Ekaterina Pomerantseva, where his research focused on investigating the performance of tunnel structured manganese oxides for electrochemical energy and water treatment applications.</p>
	<p>Dr. David Pinto received his Engineering and PhD degrees in Materials Science (Physic and Chemistry of Materials) from University Pierre and Marie Curie (Paris, France). He was a post-doctoral researcher at the Laboratoire Chimie de la Matière Condensée de Paris (France) and at the Drexel Nanomaterials Institute (Philadelphia, PA, USA). His research interests and activity focus on materials for energy storage devices, in term of engineering and physico-chemistry.</p>
	<p>José Miguel Delgado Galindo received his Bachelors in Physics and Masters in Nanoscience at the University of Barcelona. He is currently a PhD student at the Barcelona University in the Energy Storage and Harvesting department at the Catalonia Institute for Energy Research (IREC), where his research interest involves understanding the interface between electrode and water-in-salt electrolytes for electrochemical supercapacitors.</p>
	<p>Dr. Jordi Jacas Biendicho obtained his PhD in Materials science and Engineering at Sheffield University working on the electrical and electrochemical characterization of electrode materials for Li-ion batteries. During his Postdoc, he developed new tools to characterize batteries in-situ using neutron diffraction at Stockholm University and the ISIS neutron facility. Dr. Jordi Jacas is currently a consolidated researcher in the Energy Storage group at the Catalonia Institute for Energy Research (IREC) working on different technologies ranging from supercapacitors to flow batteries.</p>
	<p>Xuehang Wang is currently a postdoc researcher in A. J. Drexel Nanomaterials Institute, Drexel University, US. She received her Ph.D. in chemical engineering from Norwegian University of Science and Technology, Norway in 2016. Her research interests focus on the charge mechanism of the energy storage devices, especially the electrolyte transportation at electrode-electrolyte interphases of 2D MXenes and various carbon materials.</p>

	<p>Dr. Cristina Flox is a scientific researcher at Aalto University. She received her PhD degree in Chemistry from Universitat de Barcelona (2008). Her research interest are focused on the design and synthesis of functional nanomaterials for electrochemical water splitting (HER/OER) and storage applications (redox flow batteries, and supercapacitor).</p>
	<p>Dr. Olivier Crosnier is an assistant professor at the University of Nantes (France) since 2007. He is a researcher at Institut des Matériaux Jean Rouxel (IMN). His research focuses on materials for electrochemical energy storage with particular emphasis on innovative and/or modified materials for electrochemical capacitors and related devices. He has worked on electrode materials (both positive and negative), for supercapacitors as well as Lithium and Sodium-ion batteries, from synthesis, functionalization to materials characterization. He completed his PhD in 2001 and worked as a postdoctoral fellow at the University of Waterloo (Canada) and ICMCB (Bordeaux, France). He coauthored more than 30 papers for the last ten years.</p>
	<p>Thierry Brousse is a Professor of Materials Science at the University of Nantes. He received his PhD degree in 1991. After being a chemical engineer in a company, he joined the University of Nantes in 1994. His research at IMN focuses on innovative materials for electrochemical capacitors and related devices. He is Associate Editor for the Journal of The Electrochemical Society. He has mentored 23 PhD students. With his team as well as international collaborators, he co-authored more than 160 peer-reviewed journal publications and book chapters. He is currently vice-dean of the University of Nantes in charge of Technology Transfer.</p>
	<p>Ekaterina Pomerantseva received a Ph.D. degree in Solid-State Chemistry in 2007 from Moscow State University. Prior to joining Drexel Faculty in September 2013, she held postdoctoral appointments at the University of Maryland (2010–2013) and at the University of Waterloo (2009–2010). She has co-authored over 60 journal papers. Her research interests lie in the development and characterization of novel nanostructured materials for energy storage and water treatment with the goal to better understand electrochemical processes at nanoscale. She leads the Materials Electrochemistry Group, whose research is focused on design and application of the chemical synthesis methods to obtain materials with the desired structure and electrochemical properties.</p>
	<p>Professor J.R. Morante is full professor of the Faculty of Physics of the University of Barcelona. Since 2009 he has been director of the advanced materials area of the Energy Research Institute of Catalonia, IREC, and since 2015 he was appointed as director of this institute. Currently, he is focused on the energy transfer mechanisms occurring at interfaces involving electrons, photons, phonons and chemicals. He is specialized in the development of renewable energy systems based on nano structures and their functionalization for energy storage. He has co-authored more than 600 publications, without proceedings and books, with more than 26.900 citations (h=86) according GS data base.</p>
	<p>Dr. Yury Gogotsi is Charles T. and Ruth M. Bach Chair Professor and Distinguished University Professor of Materials Science and Engineering at Drexel University in Philadelphia, USA. He also serves as Director of the A.J. Drexel Nanomaterials Institute. His research group works on nanostructured carbons, 2D carbides and nitrides, as well as other nanomaterials for energy, water and biomedical applications. He has co-authored 2 books, 16 book chapters, more than 600 journal papers, edited 14 books, and obtained more than 50 patents. He was recognized as Highly Cited Researcher in Materials Science and Chemistry (Web of Science) in 2014–2018. He has received numerous national and international awards for his research. He also serves on the MRS Board of Directors and acts as Associate Editor of ACS Nano</p>