The critical role of point defects in improving the specific capacitance of δ-MnO₂ nanosheets

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3D porous nanostructures built from 2D δ-MnO₂ nanosheets are an environmentally friendly and industrially scalable class of supercapacitor electrode material. While both the electrochemistry and defects of this material have been studied, the role of defects in improving the energy storage density of these materials has not been addressed. In this work, δ-MnO₂ nanosheet assemblies with 150 m² g⁻¹ specific surface area are prepared by exfoliation of crystalline KₓMnO₂ and subsequent reassembly. Equilibration at different pH introduces intentional Mn vacancies into the nanosheets, increasing pseudocapacitance to over 300 F g⁻¹, reducing charge transfer resistance as low as 3 Ω, and providing a 50% improvement in cycling stability. X-ray absorption spectroscopy and high-energy X-ray scattering demonstrate a correlation between the defect content and the improved electrochemical performance. The results show that Mn vacancies provide ion intercalation sites which concurrently improve specific capacitance, charge transfer resistance and cycling stability.

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Manganese dioxide (MnO$_2$) in its many forms has been the subject of much study for electrochemical capacitor applications$^{1,2}$. In general, supercapacitors can be classified into two types: (i) electrical double-layer capacitors, which depend on charge separation at the electrode/electrolyte interface without Faradic process; and (ii) pseudocapacitors, which depend on Faradic redox reactions$^{3-5}$. ‘Extrinsic’ pseudo-capacitance has recently emerged as a subclassification of materials that host ion intercalation but are engineered to short length scales to reduce diffusion distances such that the discharge behaviour becomes linear and no structural phase changes occur$^{6,7}$.

The birnessite form of MnO$_2$ (δ-MnO$_2$), comprising stacked sheets of edge-shared MnO$_6$ octahedra with interlayer alkali ions$^{8-10}$, has been studied for some time and shows both double-layer and Faradaic charge storage$^{11,12}$. Two-dimensional (2D) δ-MnO$_2$ generally exhibits improved capacitance and rate behaviour compared to other polymorphs because the interlayer galleries provide high-speed pathways for diffusion of protons or alkali cations during the charge and discharge processes$^{13-15}$. However, the low electrical conductivity of δ-MnO$_2$ (10$^{-5}$ to 10$^{-6}$ S cm$^{-1}$) has greatly limited its application$^{16}$, prompting study of composite electrodes containing graphene$^{17,18}$, carbon nanotubes$^{19,20}$, carbon fibres$^{21,22}$ and so on. In addition, nanostructuring has been employed to improve the surface area and capacitance, for example by growing nanoneedles$^{23}$, nanoflowers$^{24}$, nanoparticles$^{25}$ and so on.

In recent years, intentional creation of cation vacancies has been explored to increase the charge storage capacitance of transition metal oxides, where cation vacancies provide additional cation intercalation sites$^{26}$. Cation vacancy content may be controlled via aliovalent cation substitution$^{27}$, anion substitution$^{28}$, reducing or oxidizing heat treatments$^{29}$, or by equilibrating the oxides in pH-controlled suspensions$^{30}$. The first studies correlating cation vacancies and charge storage properties were published by Ruetschi in the mid-1980s for intergrowth γ-MnO$_2$ phases$^{31-33}$. Metal vacancy content can be quite large in some cases, for example, Wei et al.$^{34}$ modified anatase TiO$_2$ with monovalent F$^-$ and OH$^-$ anions to form up to 22 at% V$_{Mn}$ for additional Li storage. Similarly, Koo et al.$^{34,35}$ transformed Fe$_2$O$_4$ (spinel) into hollow γ-Fe$_2$O$_3$ rods containing up to 44% vacant iron sites, and showed that Li and Na ion intercalation is possible without structural phase transformations.

Little work on the formation of cation vacancies in δ-MnO$_2$ nanosheets has been reported to date, but extensive study of the important role of birnessite-like MnO$_2$ in photosynthesis, ion sorption and other bio- and geochemical processes provides rich literature on its behaviour in aqueous environments$^{36}$. Most recently, Manceau et al.$^{30}$, building from many earlier works on Mn oxidation state in K-birnessite$^{10,37}$, systematically investigated the effects of pH on cation vacancy content in phyllosilicate nanoparticles. Their approach exploited high-energy X-ray scattering to perform pair distribution function (PDF) analysis, truncation rod analysis and simulations using the Debye equation to show that lower pH causes migration of Mn from the MnO$_2$ nanosheet to the sheet surface. Thus, the authors were able to quantify Mn vacancies in the nanosheets and Mn$^{3+}$ cations displaced to the interlayers. Later work by Marafatto and coworkers$^{38}$ employed sub-picoscopic optical and X-ray absorption spectroscopy to track the mechanisms of Mn reduction under illumination to quantify the effects of different interlayer cations on MnO$_2$ photo-reduction rates. Their results support the Mn redox reaction mechanism proposed by Manceau et al.$^{30}$, including displacement of the Mn$^{3+}$ cation to the interlayer gallery.

Additional recent work has been focused on determining mechanisms of charge storage. For example, in situ X-ray absorption studies have been used to show when the Faradaic reactions occur in MnO$_2$ nanosheets$^{38}$ and to track the average Mn oxidation state across wide voltage swings$^{39-41}$. Similarly, in situ Raman spectroscopy has been applied to track changes in the vibrational bands and has highlighted cation size effects over the Li, Na and K series$^{42}$.

In the present work, we exfoliate and reassemble δ-MnO$_2$ nanosheets to form 3D macroporous pseudocapacitive electrodes with controlled concentration of Mn point defects and Mn$^{3+}$/Mn$^{4+}$ ratios. Electrochemical and high-energy X-ray scattering measurements provide direct evidence that intentional Mn ion defects and Mn reduction synergistically improve supercapacitor performance. The three-dimensional (3D) assembly and defect control represent straightforward and industrially scalable approaches to improving specific capacitance.

**Results**

**Phases and microstructure**

The morphologies of pristine K$_2$MnO$_3$, and its protonated form, H$_2$MnO$_3$, are shown in Supplementary Fig. 3. From Supplementary Fig. 3a,b it can be seen that the K$_2$MnO$_3$ and H$_2$MnO$_3$ particles are platy, with lateral dimensions in the range of one micron, and that proton exchange does not alter the grain morphology. High-magnification SEM and TEM images are shown in Fig. 1a–c for an individual nanosheet (Fig. 1a,b) and the reassembled MnO$_2$ nanostructure (Fig. 1c). The images demonstrate that the sheets are generally flat, with some scrolled at the edges as has been noted in other nanosheet studies$^{43,44}$. The atomic force microscopy (AFM) image in Supplementary Fig. 4 also displays nanosheet fragments with flat surfaces and thickness of five nanosheets, suggesting that some of the nanosheets exfoliate into bunches or restack to a small extent upon drying. The flocculated nanosheet samples exhibit 3D porous nanostructures (Fig. 1d; Supplementary Fig. 3c) and equilibration at different pH values have no influence on their morphologies. The observation of porous structures after reassembly highlights the usefulness of our ultrasonic-assisted exfoliation and flocculation procedure, where the exfoliation rate is greatly enhanced compared with other reported procedures$^{35,46}$.

Synchrotron diffraction data for the parent K$_2$MnO$_3$ is shown in Supplementary Fig. 5. Rietveld refinement reveals that the as-synthesized parent material is layered birnessite, primarily exhibiting the monoclinic polytype with less than 10 wt% of the rhombohedral polytype and no additional crystalline phases. The X-ray diffraction patterns (Fig. 2) for protonated and reassembled MnO$_2$ demonstrate that phase purity was achieved during synthesis and that exfoliation and reassembly yields complex nanostructures as evidenced by peak broadening and asymmetry. After reassembly of the nanosheets, in-plane $h$/$k$0 reflections remain discernible, indicating that the crystalline nature of the 2D sheets is preserved. Further, the derived PDF is consistent both with literature$^{47}$ and the calculated PDF of a single δ-MnO$_2$ nanosheet (Supplementary Fig. 6), further confirming the δ-MnO$_2$ nanosheet motif is maintained. The broadening of the 00l basal reflections shows that although some sheet-to-sheet restacking occurs, the stacks are on the order of only 3–4 nm (estimated using the Scherrer equation), which is consistent with the AFM results. Shifts of the basal reflections result from increased water content in the reassembled nanosheet flocules compared with the proton-exchanged form.

Nitrogen adsorption–desorption isotherms were used to quantify the specific surface area (SSA) of all specimens as shown in Fig. 3. While protonated MnO$_2$ showed no evidence of...
mesopores, the reassembled MnO₂ nanostructures show typical type IV isotherms (IUPAC classification) with distinct H₃-type hysteresis loops, a result of open slit-like mesopores 48. The Brunauer Emmet and Teller (BET) SSA were 120 ± 0.4 m² g⁻¹ for the pH = 2 sample and 144 ± 1 m² g⁻¹ for the pH = 4 sample, and only 4.5 ± 0.1 m² g⁻¹ for H₂MnO₂, where the former values are roughly double the surface areas reported by Song et al. 49 for reassembled oxide nanosheets. Altogether, the XRD, BET and microscopy show that the reassembled nanosheets have macroand mesopores, with the mesoporosity arising due to loose agglomeration of randomly oriented sheet clusters. The extent of exfoliation and/or restacking, typical sheet thicknesses determined by AFM and average crystallinity in the sheet stacking direction as determined by XRD are similar or better for our MnO₂ specimens than those reported recently for MnO₂, TiO₂, Co₃O₄, ZnO and WO₃, for example 44. Therefore, the typical structures in Fig. 1d are of the form of edge-to-face assembled nanosheet booklets, with ‘wall thicknesses’ of up to 4 nm. The high SSA of the MnO₂ nanosheet assemblies facilitates infiltration of the electrolyte into the porous electrode to enhance the specific capacitance 6, 50.

Figure 1 | Electron microscopy of δ-MnO₂ nanosheets. (a) SEM image and (b) bright-field TEM image of exfoliated MnO₂ nanosheets, (c) high-magnification SEM image and (d) SEM image of reassembled MnO₂ nanostructures treated in pH = 2 solution for 24 h. Scale bar, 50 nm (a-c); 500 nm (d).

Figure 2 | Powder diffraction patterns of protonated and reassembled δ-MnO₂. XRD patterns of (a) protonated MnO₂, (b) reassembled MnO₂ treated in pH = 2 solution for 24 h, (c) reassembled MnO₂ treated in pH = 4 solution for 24 h. Data collected on APS 11-ID-B.

Figure 3 | N₂ adsorption isotherms of protonated and reassembled δ-MnO₂. N₂ adsorption-desorption isotherms of (a) protonated MnO₂, (b) reassembled MnO₂ treated in pH = 2 solution for 24 h, (c) reassembled MnO₂ treated in pH = 4 solution for 24 h. Curves (b) and (c) are offset by 50 and 200 cm³ g⁻¹ STP, respectively.
Redox and defects. The oxidation state of the Mn ions in all samples was investigated using Mn K-edge X-ray absorption near-edge spectroscopy (XANES) and XPS. The XPS analysis is described in Supplementary Information (Supplementary Fig. 11). Figure 4a shows the edge spectra of standard materials including MnO, Mn₃O₄, Mn₂O₃ and MnO₂.

The XANES spectra of the H₂MnO₄, pH = 2 and 4 nanosheet assemblies, and reference materials Mn₂O₃ and MnO₂ are shown in Fig. 4b. The line profiles are characterized by features that correspond to a pre-edge range with two weak broad peaks at 6,540–6,545 eV, a main-edge range that has one inflection point A, and the resonance peak range B.²⁹,₃₃ The weak pre-edge peaks P and P' correspond to the dipole-forbidden 1s → 3d transition.²⁴ All three samples exhibit higher intensity of peak P' than for peak P, but the peak P' is less intense as compared with the β-MnO₂ reference. This observation confirms the existence of mixed oxidation states of Mn³⁺/Mn⁴⁺ in the samples. Also, the higher intensity ratio of P' to P for H₂MnO₄ compared with the pH = 2 and 4 samples indicates that it has less Mn³⁺, because the relative intensity of the peaks P'/P is proportional to the average oxidation state.²⁴

The main absorption range can be assigned to the dipole-allowed 1s → 4p transition. The associated edge energy is usually taken as the energy of the peak in the first derivative, which corresponds to the inflection point of the main edge in the XANES spectra (Fig. 4c). Clearly, the main absorption edge (A) progressively shifts to lower energies with decreasing pH, implying lower pH progressively reduces Mn to the trivalent state. Also, the presence of the intense peak B for the nanosheet assemblies indicates that they are mainly comprised of edge-shared MnO₆ octahedra.⁵⁵ This observation further confirms that the δ-MnO₂ lattice is not dissolved by equilibration in HCl at pH as low as 1.

The average oxidation state (AOS) of Mn was determined by establishing a linear relationship between the K-edge energy and Mn oxidation state (Fig. 4d). The AOS of Mn is 3.59 for H₂MnO₄, 

![Figure 4](image-url)
I(Q) and MDO samples studied herein, we find that treating the exfoliated tool for investigating the structures of poorly-crystalline materials intermediate and long-range order, thus making it an appropriate probes not only the local atomic bonding motifs but also specific goal of correlating the quantity of Mn point defects with either surface water or Mn. The inverse trends in the Mn–Mn peak (2.89 Å) and Mn–MnIL peak (3.45 Å) as a function of pH support the Mn3+

The interactions of neighbouring in-plane Mn3+ and of preventing displacement of Mn3+ (pH treated at higher pH have AOS values of 3.59, whereas the exfoliated samples treated at higher pH have AOS values of 3.36 (pH = 4) and 3.24 (pH = 2). We attribute the lesser extent of Mn reduction in crystalline H3MnO2 to steric hindrance by the interlayer galleries which are crowded with protons and water. This has the two-fold effect of hindering access of aqueous H3O\(^+\) to reducible Mn4+, and of preventing displacement of Mn3+ to the sheet surface. Indeed, earlier work by Gailloit et al.\(^{30}\) noted that during thermal reduction of Mn4+ in crystalline K-birnessite, Mn vacancies were not formed despite the unfavourable in-sheet lattice strain due to Jahn–Teller distortions inherent to Mn3+. The interactions of neighbouring in-plane Mn3+ and Mn4+ sites therefore contributes both strain and electrostatic-driven components to the energetics of δ-MnO2 defect equilibration.

High-energy X-ray scattering and pair distribution function analysis were undertaken to further characterize the defects formed in soft chemically reduced MnO2 nanosheets, with the specific goal of correlating the quantity of Mn point defects with Mn reduction and electrochemical performance. PDF analysis probes not only the local atomic bonding motifs but also intermediate and long-range order, thus making it an appropriate tool for investigating the structures of poorly-crystalline materials and nanoparticles that yield diffraction patterns with large amounts of diffuse scattering\(^{47}\).

The observed scattered intensity, the reduced structure function F(Q) and the associated PDF for the reassembled nanosheets assemblies, and (c) G(r) for the pH-treated samples, protonated MnO2 (H4MnO2), and parent phases (KxMnO2). The basal reflections evident in I(Q<2 Å\(^{-1}\)) indicate a measure of restacking. The variation in intensity as a function of pH indicates a variation in the interlayer structure attributable to either surface water or Mn. The inverse trends in the Mn–Mn peak (2.89 Å) and Mn–MnIL peak (3.45 Å) as a function of pH support the Mn3+

Comparison of defect structures and electrochemical supercapacitor properties of bulk protonated H3MnO2 and MnO2 nanosheet assemblies.

Table 1 | Summary findings of defects and electrochemistry in δ-MnO2 electrodes.

| Samples          | AOS [Mn3+ (%)] | [Mn4+ (%)] | [Vsurf] (%) | S.S.A. (m² g⁻¹) | C\(_{\text{c}}\) (F g⁻¹) | R\(_{\text{ct}}\) (Ω) | Na : Mn (frac.) |
|------------------|----------------|------------|-------------|-----------------|----------------|----------------|----------------|
| Reassembled MnO2 - pH 2 | 3.24          | 76         | 24          | 26.5            | 120            | 306            | 3              | 0.28           |
| Reassembled MnO2 - pH 4 | 3.36          | 64         | 36          | 19.9            | 144            | 209            | 15             | 0.19           |
| Protonated MnO2  | 3.59          | 41         | 59          | 18.3            | 4.5            | 103            | 23             | 0.09           |

Where the superscript 0 denotes quantities in KxMnO2, the subscript s denotes quantities for a derivative sample, and [Mn]\(^{0}\) is taken as 1. The absolute accuracy of the values obtained using equation (1) will be influenced by the correlations between interlayer water or hydroxyl pairs, which perturb the low-r PDF region, leading to overestimation of the Mnsurf content\(^{47}\). While there is notable difficulty in absolute quantification of Mn defects in these materials, this method should provide reasonable relative quantification in the derived nanosheet assemblies.
Although estimation of error is not possible with this empirical approach, a per cent level of uncertainty is expected for the calculated Mn concentrations.

As shown in Fig. 6a, the \( V_{\text{Mn}}^{\text{surf}} \) concentration, which is equivalent to the \( M_{\text{Mn-surf}}^{\text{surf}} \) concentration, is then \( 1 - [\text{Mn}] \) in fractional units. Here we define this type of defect as a ‘surface Frenkel’ defect, where displacement of the in-plane Mn to the nanosheet surface is reminiscent of the Frenkel defect vacancy-interstitial pair. The results of our analysis are summarized in Table 2. Consistent with the model of Manceau et al.,

we observe an increase in \( V_{\text{Mn}}^{\text{surf}} \) with decreasing pH, as well as the appearance of a PDF peak at a distance not found in the \( \delta\text{-MnO}_2 \) structure, which corresponds to a Mn–Mn surf. The increase in concentration of surface Frenkel defects by \( \sim 30\% \) between the pH = 4 and pH = 2 samples supports the hypothesis that increased proton sorption at the MnO2 surface in more acidic electrolytes expels more in-plane Mn leading to the formation of more Mn vacancies.

As noted for the Mn valence, the PDF analysis likewise shows an apparent contradiction in the surface Frenkel defect content of the crystalline H₃MnO₂ when compared to the defect content of the pH = 2 and 4 samples. As shown in Table 1, while the protonated form H₃MnO₂ is equilibrated at pH < 1, its defect concentration (18.3%) is smaller than that in the pH = 2 sample (26.5%) and is even smaller than that of the pH = 4 sample (19.9%). As noted earlier, previous work shows that Mn⁴⁺, with its Jahn–Teller distortion, may be accommodated in MnO₂ sheets in crystalline birnessites. Table 1 shows that \( \sim 2/3, 1/2 \) and // of the Mn ions remaining in the nanosheets are reduced to Mn⁴⁺ for the pH = 2, 4 and H₃MnO₂ samples, respectively. The PDF and XANES analyses are therefore complementary in demonstrating that surface Frenkel defects and Mn reduction are more favourable in high-surface area nanosheet assemblies, with steric limitations reducing the extent of the reactions in well-crystalline birnessites.

**Figure 6 | Empirical analysis of \( \delta\text{-MnO}_2 \) PDF.** Using the resolved in-plane Mn-Mn correlation peak (a) we can empirically estimate the Mn surface Frenkel (circled) concentration using a Gaussian peak and linear baseline (b). The PDF amplitude is normalized to the Mn–O correlation peak; therefore the ratio of nanosheet Mn-Mn to \( K\text{MnO}_2 \) Mn-Mn peak areas represents the fractional Mn-occupancy of the nanosheet assembly. \( \delta\text{-MnO}_2 \) equilibrated at pH = 2 is shown here.

**Table 2 | Estimation of surface Frenkel defect concentration.**

| Data set          | Centre (Å) | Height (arb.) | Area (arb.) | FWHM (Å) | Mn-vac. (%) |
|-------------------|------------|---------------|-------------|-----------|-------------|
| Pristine MnO₂     | 2.897      | 15.988        | 3.461       | 0.203     | N/A         |
| Protonated MnO₂   | 2.858      | 13.896        | 2.826       | 0.191     | 18.3        |
| Reassembled MnO₂–pH 4 | 2.876 | 13.810        | 2.772       | 0.189     | 19.9        |
| Reassembled MnO₂–pH 2 | 2.867 | 12.335        | 2.544       | 0.194     | 26.5        |

Gaussian parameters for the Mn–Mn in-sheet PDF peak corresponding to different samples extracted using Fityk. Peak area is normalized to the Mn vacancy content of the parent phase K₆MnO₂ with the assumption that the intrinsic [V₆Mn] population is on the order of parts per million in the high-temperature crystalline phase.
68% of its initial capacitance. Our ongoing work involves tracking the reversibility of the electrochemical strains induced during cycling, and although we have not yet uncovered the origins of the cycling fade, our results are promising when compared with earlier work, for example for MnO₂ nanostructures which retain 92% of the initial capacity after 1,000 cycles when using a current density five times smaller.\(^{49}\)

Electrochemical impedance spectroscopy (EIS) was employed to measure the charge transfer resistance of each electrode with the results shown in Fig. 8a. All plots exhibit a straight line in the low-frequency region and a single semicircle in the high-frequency region, indicating a diffusion-limited step in the low frequency region and a charge transfer limited step in the high-frequency region.\(^{60}\) The Nyquist plots were further modelled and interpreted by using an appropriate electrical equivalent circuit, which is shown in the inset in Fig. 8a. \(R_s\) is a combined resistance including ionic resistance of the electrolyte, intrinsic resistance of the substrate and contact resistance at the active material/current collector interface. \(R_{ct}\) is the charge transfer resistance caused by the Faradaic reaction. \(Z_w\) is the Warburg resistance which is related to ion diffusion in the electrolyte, \(CPE\) is a constant phase element and \(C_L\) is the limit capacitance.\(^{61–63}\) The calculated charge transfer resistances \((R_{ct})\) extracted from the high-frequency range were 23, 15 and 3 \(\Omega\) for...
the H₂MnO₂, pH = 4 and pH = 2 samples, respectively, as shown in Fig. 8b.

Table 1 summarizes the characteristics of the electrodes and their properties, showing several clear trends. First, the XPS and XANES studies, combined with quantification of surface Frenkel defects, demonstrate that the Mn³⁺/Mn⁴⁺ ratio in the nanosheets trends with pH treatment. More specifically, Mn⁴⁺ → Mn³⁺ reduction does not only result in formation of surface Frenkel defects but some of the Mn within the sheets is reduced to the trivalent state. As calculated based on the data in Table 1, ~2/3, 1/2 and 1/4 of the Mn ions remaining in the nanosheets are reduced to Mn³⁺ for the pH = 2, 4 and H₂MnO₂ samples, respectively.

The specific capacitance for the assembled nanosheets correlates with the surface Frenkel defect population and Mn³⁺ content, as well as charge transfer resistance. For example, the surface areas of the pH = 2 and 4 samples are similar, but the sample treated at pH = 2 has 50% higher capacitance, 47% more Na⁺ ion intercalation, × 5 smaller charge transfer resistance, with 93% less surface Frenkel defects, highlighting the importance of the cation defects on Na⁺ ion intercalation.

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Discussion

Electrostatic assembly of δ-MnO₂ nanosheets in suspension under carefully controlled experimental conditions yields self-assembled 3D porous nanostructures with surface areas of ~150 m²g⁻¹. Equilibrating the reassembled nanosheets in varied pH controls the extent of Mn⁴⁺ → Mn³⁺ reduction, as well as creating charged defect pairs we term 'surface Frenkel defects' comprising a Mn vacancy within the sheet and a six-fold coordinated Mn³⁺ site on the surface of the nanosheet. The Mn surface Frenkel defect content reaches 26.5% for the nanosheet assemblies equilibrated at pH = 2 and 19.9% for the pH = 4 sample. The XPS and XANES data indicate an increase of the Mn³⁺/Mn⁴⁺ ratio with decreasing pH and the electrochemical results show direct correlation of Mn cation defects with specific capacitance. The specific capacitance increased from about 200 F g⁻¹ (pH = 4) to over 300 F g⁻¹ (pH = 2) by intentional introduction of ~30% surface Frenkel defects, while at the same time the charge transfer resistance decreased from ~15 Ω to ~3 Ω. Therefore, it is now clear that Mn surface Frenkel defects in δ-MnO₂ nanosheets increase Na⁺ ion intercalation by providing new, low energy intercalation sites.

Methods

Chemicals and reagents. MnCO₃, K₂CO₃, Na₂SO₄, acetylene black, poly(vinylidene fluoride) (PVDF) and nickel foil were purchased from Alfa Aesar. 6N hydrochloric acid (HCl) solution and sodium hydroxide (NaOH) were obtained from Fisher Scientific. The tetrabutylammonium hydroxide solution (TBAOH, 40 wt% in H₂O) and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich. All reagents were used as received without further purification.

Fabrication of δ-MnO₂ nanomaterials. Powder synthesis included mixing MnCO₃ and K₂CO₃ powders in a molar ratio of 40 : 9, by milling in isopropyl alcohol. Then 0.01 mol of MnCO₃ was disintegrated using a MeadOne Ball Mill. The resultant suspension was dried at a hot plate for 30 min at 60 °C and then calcined in alumina crucible at 800 °C for 24 h in air. 0.5 g of the resulting layered K₂MnO₃ was proton ion-exchanged in HCl solution (1 mol l⁻¹, 45 ml) in an ultrasonic bath at room temperature for 4 h. The ion exchange process was repeated two additional times, followed by washing with DI water and air drying. The absence of K ions was confirmed by energy dispersive spectroscopy and XPS survey scans shown in Supplementary Figs 1 and 2. In addition, the XPS survey scans showed a complete absence of any signal from Al ions, giving good confidence that no contamination by the Al₂O₃ milling media was encountered.

Characterization of the samples. Microstructures were studied using scanning electron microscopy (SEM, FEI Quanta 200) at 20 kV. Transmission electron microscopy and high-resolution TEM were carried out using a Hitachi HF-3300 TEM/STEM. The STEM unit has a secondary-electron detector, which allows simultaneous high-resolution TEM and SEM imaging at 300 kV. The thickness and crystalline diameter of the exfoliated MnO₂ nanosheets were probed by micro-diffraction atomic force microscopy (AFM, Bruker D8000), X-ray photoelectron spectroscopy (XPS, PHI Quantera X-ray photoelectron spectrometer equipped with Al Kα radiation) and energy-dispersive X-ray spectroscopy (EDX, EDAX Genesis). The exfoliation process was controlled using antimony doped silicon tips. The exfoliated nanosheets were electrostatically attached to a clean silicon wafer by drying the nanosheet suspension, and imaged in air. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 DTA/TGA under flowing air with a heating rate of 10 °C min⁻¹. The presence of any functional groups from organic compounds was probed with infrared spectroscopy ( Nicolet 6700 FT-IR Spectrometer, USA).

The specific surface area and porosity were examined by nitrogen adsorption and desorption isotherms collected at 77 K using a Micromeritics TriStar II 3020 system. The local chemical environment of the samples was characterized using a monochromatic X-ray photoelectron spectrometer equipped with a Si monochromator, and the software package ATHENA was used for analysis. The Mn vacancy content in δ-MnO₂ samples was determined using high-energy X-ray scattering and PDF analysis, with data collected at the Advanced Photon Source on beam-line 11-ID-B using the rapid-acquisition PDF method. Data sets were collected using standard 1 mm Kapton capillaries in a glovebox under flowing argon, and the software package Athena was used to refine the X-ray scattering data. Scattering data for PDF extraction were collected over a Q-range of 0.4–24.5 Å⁻¹, and the powder diffraction data for all samples was collected over a Q-range of 0.2–9.0 Å⁻¹. 2D X-ray diffraction data were integrated to 1D using FIT2D, after appropriately correcting detector deviations from orthogonality and masking invalid pixels. CeO₂ was used as the calibration standard for detector geometry. Meanwhile, CeO₂ and Ni were used to evaluate the instrument response function. The PDF data was reduced using PDFgetX2 (ref. 69), which includes the appropriate corrections for inelastic scattering and energy-dependent detector response, in addition to experimental background and absorption corrections, amongst others.

Electrochemical measurements. The working electrode was prepared by mixing 80 wt% active material, 15 wt% acetylene black and 5 wt% PVDF in NMP solution. After stirring for 6 h, the homogeneous slurry was spread onto a Ni foil substrate with an area of 1 cm², and then heated at 100 °C for 2 h to evaporate the solvent and obtain the electrode. The loading of the active material on the working electrode was in the range of 0.5–0.6 mg cm⁻². The capacitive performance was measured using a CHI 600E electrochemical analyser (CHE, USA) with a conventional three-electrode cell. Ag/AgCl and platinum wire were used as the reference and auxiliary electrodes, respectively, with 1 M Na₂SO₄ aqueous.
electrolyte. Cyclic voltammetry scans were carried out from 0 to 1 V at a scan rate of 50 mV s−1. Galvanostatic charge–discharge was measured at different constant current densities from 0.2 to 10 A g−1. EIS was performed in the frequency range of 0.1 Hz–100 kHz at an open circuit potential of 5 mV. EIS data was fitted to an equivalent electrical circuit model using ZsimpWin (Version 3.21, EChem Software) software.

Data availability. The data that support the findings of this study are available from the authors on request.

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Author contributions

S.T.M., D.L. and D.D.E. conceived the research. P.G. and T.H. synthesized the materials. P.G. performed the electrochemical measurements. P.M. and S.T.M. performed the X-ray scattering measurements. P.G. and R.H. performed the XANES measurements. Y.G. performed the XPS and AFM measurements. J.Y.H. performed the TEM measurements. P.G., P.M. and T.H. performed the material characterization. All authors discussed and analysed the data. P.G., P.M. and S.T.M. wrote the paper. All authors discussed and commented on the manuscript.

Additional information

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