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# Electrochemical performance and structural evolution of spray pyrolyzed $\text{Mn}_3\text{O}_4$ thin films in different aqueous electrolytes: effect of anions and cations†

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This work presents the impact of cycling in different cationic and anionic aqueous electrolytes on the electrochemical storage performance of the  $\text{Mn}_3\text{O}_4$  thin film electrode prepared using the chemical pyrolysis method. Studies on the as-deposited electrode confirmed the formation of  $\text{Mn}_3\text{O}_4$  phase. Extensive electrochemical analysis was performed using  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MgSO}_4$  electrolytes to examine the influence of cations and anions on charge storage behaviour. Considerable changes were observed in the specific capacitances owing to different ionic sizes as well as hydrated ionic radius of the electrolyte ions. Accordingly, the electrode unveiled a good performance showing a specific capacitance of around  $187 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  in  $\text{K}_2\text{SO}_4$  electrolyte. Further, the electrode properties are examined after 500 CV cycles to trace the changes in the structural and morphological properties. X-ray diffraction (XRD) and Raman spectroscopic studies illustrate a partial phase transformation of electrodes from  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}_2$  irrespective of the electrolytes. These results are further corroborated with X-ray photoelectron spectroscopic (XPS) analysis where there was an increment in the oxidation state of manganese. It has been observed that the surface properties were significantly changed with cycling, as manifested by the wettability studies of the electrodes. The obtained results brings out the significance of electrolyte ions on the charge storage characteristics of  $\text{Mn}_3\text{O}_4$  thin film electrodes in light of their possible application in electrochemical capacitors.

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## 1. Introduction

In the realm of energy storage, supercapacitors (SCs) or electrochemical capacitors (ECs) play a pivotal role owing to their high power density, high cyclic stability, fast charge/discharge rate, moderate energy density, *etc.*<sup>1–4</sup> Compared to other front-runners in the field, such as conventional capacitors and batteries, supercapacitors cover a large area on the Ragone plot, making them highly significant in the research community.<sup>5</sup> From the viewpoint of storage mechanism, SCs are classified as electric double-layer capacitors (EDLCs), pseudocapacitors (PCs), and hybrid capacitors.<sup>6</sup> In EDLCs, storage is achieved through the electrostatic attraction of electrolyte ions on the

electrode surface, which is a non-faradaic process. In contrast, PCs operate *via* fast redox reactions occurring at the interface of electrode and electrolyte, characteristic of faradaic processes. Hybrid capacitors synergistically incorporate both faradaic and non-faradaic processes, combining the benefits of electrostatic charge accumulation with rapid redox reactions.<sup>7–9</sup> Transition metal oxides (TMOs) and conducting polymers are among the primary electrode options employed in pseudocapacitors.<sup>10,11</sup> TMOs are particularly advantageous due to their cost effectiveness, superior electrical conductivity, as well as excellent electrochemical stability, and the potential to afford higher energy density.<sup>12</sup> Additionally, TMOs exhibit a variety of oxidation states and possess rich redox chemistry, enabling diverse and efficient energy storage mechanisms.<sup>13</sup> To date, various studies have been performed on many TMOs to assess their suitability as potential electrode materials. Among these, manganese oxide is regarded as one of the promising candidate as it has very good electrochemical behaviour alongside their cost-effectiveness and environmental friendliness.<sup>14,15</sup> They have a variety of phases due to their multiple oxidation states, among which  $\text{Mn}_3\text{O}_4$  (hausmannite) is most stable at higher temperatures.  $\text{Mn}_3\text{O}_4$  usually finds applications in catalysis, Li-ion

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batteries, supercapacitors *etc.*<sup>16–19</sup> Moreover, the mixed valence of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  in  $\text{Mn}_3\text{O}_4$  results in rich redox chemistry with high theoretical capacitance.<sup>20,21</sup>

However, it is a familiar fact that the specific capacitance of an electrode is also altered by the type of electrolyte used.<sup>22–24</sup> It has been observed that electrodeposited  $\text{Mn}_3\text{O}_4$  exhibited great pseudocapacitance and stability over a potential window of  $-0.1$  V to  $1$  V in  $1$  M  $\text{Na}_2\text{SO}_4$  compared to  $1$  M  $\text{NaOH}$  and  $1$  M  $\text{KOH}$  mixed with  $0.04$  M  $\text{K}_4\text{Fe}(\text{CN})_6$ .<sup>25</sup> This is because, when  $\text{Na}_2\text{SO}_4$  is used as the electrolyte, the phase has been altered from tetragonal  $\text{Mn}_3\text{O}_4$  to tetragonal  $\text{MnO}_2$  with a significant change in the morphology as well. On the other hand,  $\text{Mn}_3\text{O}_4$  on carbon cloth (CC) showed higher specific capacitance and low resistance in  $\text{KOH}$ , while better rate capability and cyclic stability in  $\text{Na}_2\text{SO}_4$ .<sup>26</sup> The low resistance in  $\text{KOH}$  is attributed to its better ionic conductivity as compared to  $\text{Na}_2\text{SO}_4$ . In another work, the electrolyte cation effect was tested on the electrochemical activation of the  $\text{Mn}_3\text{O}_4$  electrode prepared through the hydrothermal method.<sup>27</sup> The electrode exhibited different activation or phase transitions in  $\text{Li}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{K}_2\text{SO}_4$  electrolytes. A reasonably good capacitive performance was observed in  $\text{K}_2\text{SO}_4$ , whereas poor cyclic stability was noticed in  $\text{MgSO}_4$ . Similarly,  $\text{Mn}_3\text{O}_4$  nanoparticles showed enhanced electrochemical performance in  $\text{KOH}$  electrolyte when compared with  $\text{KCl}$  because of the lesser anion size of  $\text{OH}^-$  than that of  $\text{Cl}^-$ .<sup>28</sup> Thus, it is evident that both anion and cation of the electrolyte can effectively determine the storage performance.

The charge storage mechanism in  $\text{Mn}_3\text{O}_4$  involves surface redox reactions with electrolyte ions. Many studies have been done on predicting the storage mechanism in  $\text{Mn}_3\text{O}_4$ . Previously, it was seen that, during charging  $\text{Mn}_3\text{O}_4$  nanofibers will transform into  $\text{Na}_6\text{MnO}_x \cdot n\text{H}_2\text{O}$  through surface adsorption of solvated ions.<sup>29</sup>  $\text{Mn}_3\text{O}_4$  thin films treated at a high temperature ( $900^\circ\text{C}$ ) showed a phase transformation to a layered birnessite structure by cycling in  $\text{Na}_2\text{SO}_4$  electrolyte.<sup>30</sup> This transformation brought a significant change in the specific capacitance owing to the electrochemical activation. Thus a significant research emphasis has been on the study of phase transformation upon cycling.<sup>31–33</sup> However, the impact of different electrolytes in the phase transformation is rarely investigated. On the other hand,  $\text{Mn}_3\text{O}_4$  has been synthesized in various forms including different nanostructures and thin films.<sup>34–37</sup> Most of the nanostructures are in powder form which imposes the use of binders that cause extra resistance and stability issues with the current collector.<sup>38</sup> To avoid these limitations, thin film electrodes are gaining attention which ensures good stability and shorter ion diffusion length with good charge transport.<sup>39</sup> In this direction, different synthesis techniques were explored for the preparation of  $\text{Mn}_3\text{O}_4$  thin films, involving, physical methods as well as chemical methods.<sup>40–44</sup> Spray pyrolysis is a low-cost, chemical, and solution-based technique that has a high demand when it comes to industrial purposes.<sup>45</sup> However, deposition technique significantly impact the electrode properties, mainly the morphology and other surface parameters, and to the best of our knowledge, no studies have reported on the electrochemical properties of spray-pyrolyzed thin films in different electrolytes.

From this perspective, this work focuses on understanding the consequences of various aqueous electrolytes on the electrochemical behaviour of  $\text{Mn}_3\text{O}_4$  thin film electrodes synthesized using the chemical spray pyrolysis technique. To realize a better understanding, some of the characterizations were done that promote the interpretation of electrode properties before and after electrochemical testing. Subsequently, the structural and morphological changes brought by the electrochemical testing in different electrolytes were presented.

## 2. Experimental

All the chemicals utilised were of analytical grade and used without further purification.  $\text{Mn}_3\text{O}_4$  thin film electrodes were deposited over the conducting fluorine-doped tin oxide (FTO) coated glass substrate employing spray pyrolysis technique as described in our previous work.<sup>46</sup> Initially, the substrate was subjected to cleaning through ultrasonication in isopropyl alcohol and then by UV-Ozone treatment for a time interval of  $10$  min. Manganese acetate tetrahydrate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) (Sigma-Aldrich,  $\geq 99\%$ ) was dissolved in double distilled water to make the optimized molar concentration of  $0.06$  M and the solution was made to stir at room temperature. Meanwhile, the cleaned substrate was kept on the hot plate maintained at an optimized temperature of  $325^\circ\text{C}$ . The precursor was sprayed on the hot substrate at a flow rate of  $1\text{ mL min}^{-1}$  using compressed air at a pressure of  $1$  bar as the carrier gas. The spray nozzle to substrate distance was retained at  $14.5$  cm. The active mass loading of the film was observed to be around  $0.4\text{ mg cm}^{-2}$  and the film thickness was around  $0.790\text{ }\mu\text{m}$ .<sup>47</sup> Then the films were characterized to study their structural, topographical, morphological, elemental as well as electrochemical properties. A set of electrodes was then subjected to electrochemical testing in various aqueous electrolytes. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) studies were performed in electrolytes with different anions ( $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ ) as well as different cations ( $\text{Li}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{K}_2\text{SO}_4$ ). All the electrolytes were made to the concentration of  $0.1$  M using double distilled water.

X-ray diffraction (XRD) pattern was acquired using  $\text{Cu K}\alpha$  radiation of wavelength,  $\lambda = 1.5405\text{ }\text{\AA}$  within  $2\theta$  between  $10^\circ$  to  $70^\circ$  (Rigaku Miniflex 600) to probe the structural properties of the deposited film. Raman spectrum was obtained with the Renishaw-inVia Raman microscope at the excitation wavelength of  $532\text{ nm}$ . Surface morphology studies were done using scanning electron microscopy (SEM) at an accelerating voltage of  $5\text{ kV}$  (Oxford Zeiss Sigma Microscope). Further, compositional studies were carried out through energy dispersive spectroscopy (EDS) at an accelerating voltage of  $15\text{ kV}$ . X-ray photoelectron spectroscopy (XPS) spectra were acquired using an Axis Supra spectrometer with a non-monochromatic source of  $\text{Al K}\alpha$  ( $h\nu = 1486.6\text{ eV}$ ). CASAXPS was used for the analysis with Shirley background subtraction for the charge-corrected data. Additionally, a wettability test was done to measure the contact angle using a water droplet. All electrochemical characterizations (cyclic voltammetry (CV), galvanostatic charge/discharge (GCD),



and electrochemical impedance spectroscopy (EIS)) were conducted using Metrohm, Autolab PGSTAT204 workstation in three-electrode setup with the as-prepared electrode as working electrode, Ag/AgCl as reference electrode and platinum as counter electrode. The CV tests were carried out at different scan rates ranging from 5 to 100 mV s<sup>-1</sup>, and the GCD analyses were conducted at current densities from 0.5 to 2 A g<sup>-1</sup>. The EIS measurements were conducted in the frequency range from 10 mHz to 1 MHz. All the measurements were done at ambient temperature.

### 3. Results and discussion

#### 3.1. Characterizations of the electrode before cycling

The phase as well as crystal structure of the as-prepared electrode was validated using XRD. Fig. 1a depicts the XRD pattern of the Mn<sub>3</sub>O<sub>4</sub> thin film coated over the FTO substrate. All the peaks were identified and indexed comparing with the standard JCPDS card (Mn<sub>3</sub>O<sub>4</sub>: 24-0734, FTO: 44-1445). The observed pattern resembles with the tetragonal phase of Mn<sub>3</sub>O<sub>4</sub> with the space group 14<sub>1</sub>/amd.<sup>48</sup> Major peaks at 32.8° and 36.3° is due to the reflections from (103) and (211) planes respectively. However, intense reflections from the FTO substrates also

appeared in the pattern owing to the higher penetration of X-rays. The crystallite size (*D*) was estimated utilizing Scherrer's equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \text{ (in nm)} \quad (1)$$

where  $\beta$  represents the peak broadening in radians,  $\theta$  indicates the position of the peak in radians,  $\lambda = 0.15405$  nm is the wavelength of Cu-K $\alpha$  radiation used for diffraction, and  $K = 0.9$  denotes the shape factor. The calculated *D* value was approximately 8.5 nm. Furthermore, the micro-strain ( $\epsilon$ ) and dislocation density ( $\delta$ ) were estimated employing the following relations:

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad (2)$$

$$\delta = \frac{1}{D^2} \quad (3)$$

The values obtained were approximately  $12.9 \times 10^{-3}$  and  $1.4 \times 10^{16} \text{ m}^{-2}$  respectively.

Fig. 1b illustrates the Raman spectrum of the Mn<sub>3</sub>O<sub>4</sub> electrode, revealing three characteristic vibrational modes

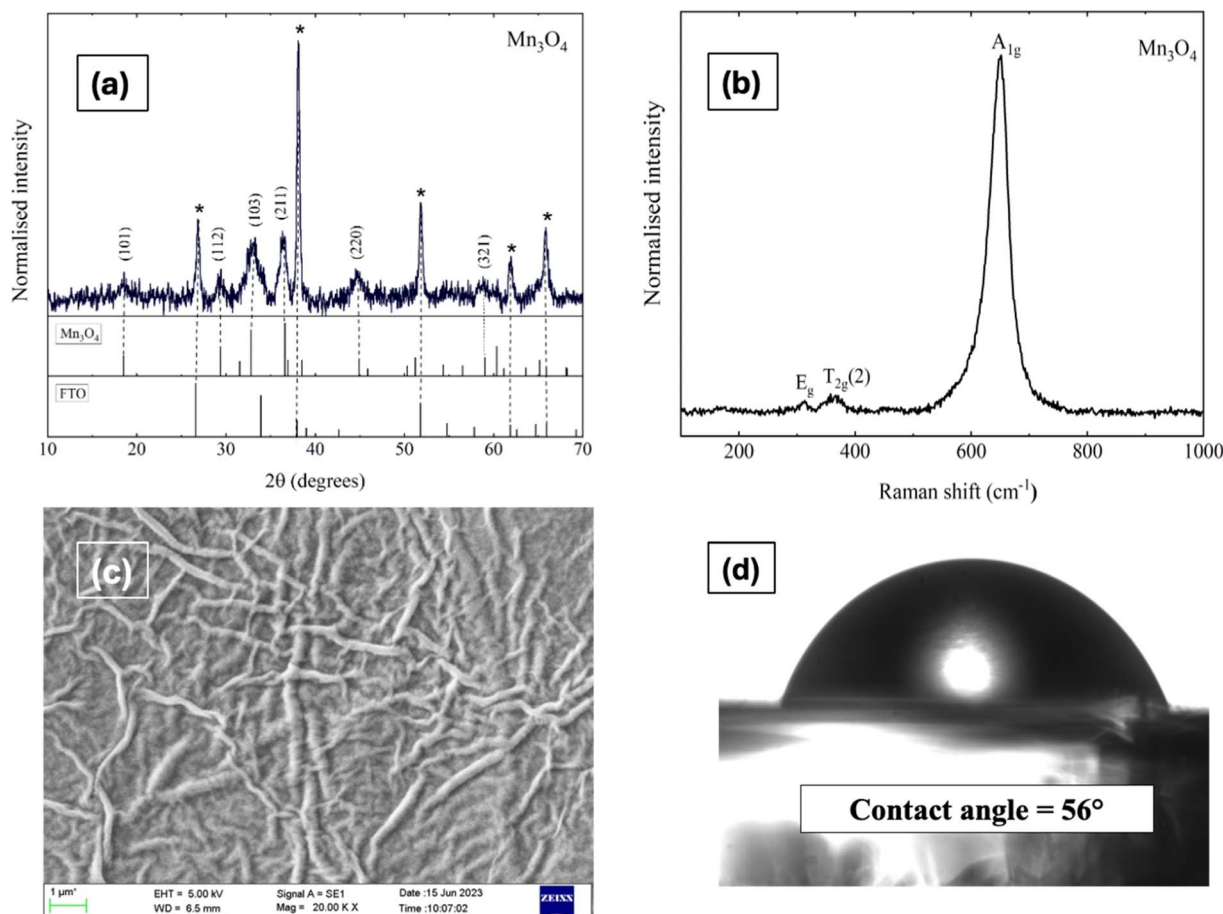


Fig. 1 (a) X-ray diffractogram, (b) Raman spectra, (c) SEM micrograph (magnification: 20KX), and (d) contact angle measurement of Mn<sub>3</sub>O<sub>4</sub> thin film electrode.



indicative of spinel  $\text{Mn}_3\text{O}_4$  formation. The peak with high intensity at  $651\text{ cm}^{-1}$  ( $\text{A}_{1g}$  mode) corresponds to the Mn–O symmetric stretching vibration, while the peaks at  $310\text{ cm}^{-1}$  and  $363\text{ cm}^{-1}$  ( $\text{E}_g$  and  $\text{T}_{2g}(2)$  modes, respectively) are attributed to the asymmetric bending vibrations of the Mn–O bond. The phase purity of the deposited film is confirmed by the absence of additional peaks in the spectrum. Fig. 1c presents the SEM micrograph (Fig. S4† shows the images with different magnifications) of the  $\text{Mn}_3\text{O}_4$  electrode, showcasing a fibre-like morphology with a uniform coating across the substrate, free of voids, cracks, or pinholes. Additionally, Fig. 1d displays the wettability test of the  $\text{Mn}_3\text{O}_4$  thin film electrode surface, indicating its hydrophilic nature with a contact angle of around  $56^\circ$ .<sup>49</sup>

### 3.2. Electrochemical characterizations: effect of electrolyte anions and cations

The impact of different electrolyte anions and cations on the electrochemical performance of the synthesized  $\text{Mn}_3\text{O}_4$  thin film electrodes was investigated using CV in a three-electrode setup.  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  were chosen as electrolytes with different anions. Fig. 2a and b represent the CV curves of the  $\text{Mn}_3\text{O}_4$  thin film electrodes in  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ , respectively,

over a potential window (PW) of  $-0.2\text{ V}$  to  $0.8\text{ V}$  at different scan rates. The electrodes demonstrated pseudocapacitive behaviour in both electrolytes, with the current increasing with the scan rate, consistent with previous CV results obtained in  $\text{Na}_2\text{SO}_4$ .<sup>46</sup> Fig. 2c compares the CVs at a scan rate of  $5\text{ mV s}^{-1}$ , showing no significant differences in shape or peak current values. From the figure, it is apparent that the oxidation and reduction processes were roughly similar in both electrolytes, regardless of the anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ). The specific capacitance was estimated by making use of the following formula:

$$C = \frac{\int I(v)dV}{mv(\Delta V)} \quad (4)$$

where  $\int I(v)dV$  implies the area enclosed under the CV curve,  $m$  denotes the active mass deposited,  $v$  refers to the scan rate and  $\Delta V$  represents the applied PW. Notably, at a scan rate of  $5\text{ mV s}^{-1}$  in  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  electrolytes, the estimated values are strikingly similar, measuring  $94\text{ F g}^{-1}$  and  $93.5\text{ F g}^{-1}$ , respectively.

To delve into the kinetic differences induced by varying anions, electrochemical impedance spectroscopic studies were executed. Fig. 3 portrays the Nyquist plots of the  $\text{Mn}_3\text{O}_4$  electrode in  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  electrolytes. It is evident from the figure that the storage kinetics were notably superior in the

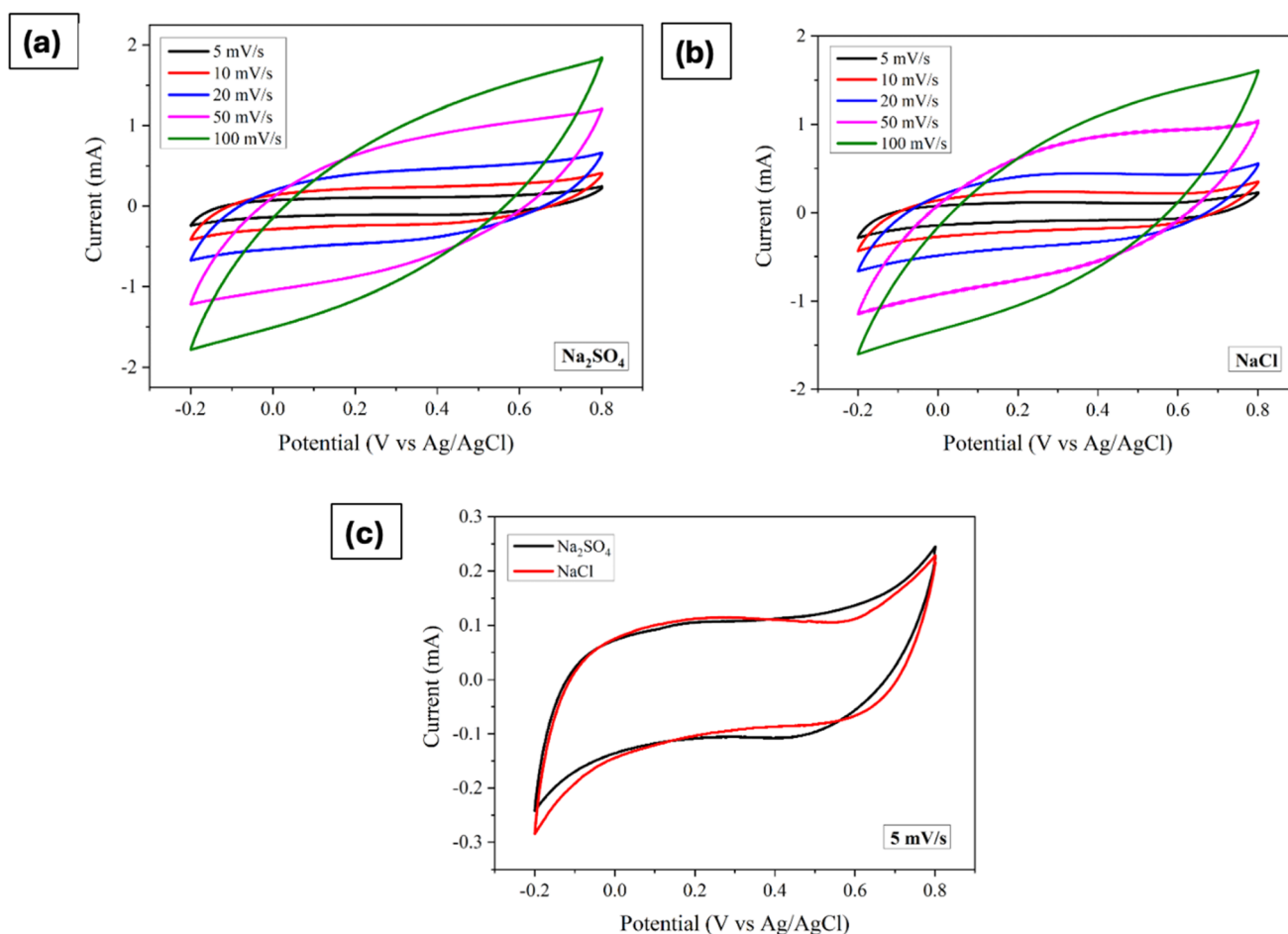


Fig. 2 Cyclic voltammograms of  $\text{Mn}_3\text{O}_4$  thin film electrode in (a)  $\text{Na}_2\text{SO}_4$ , and (b)  $\text{NaCl}$ . (c) Comparison of CVs at a scan rate of  $5\text{ mV s}^{-1}$ .



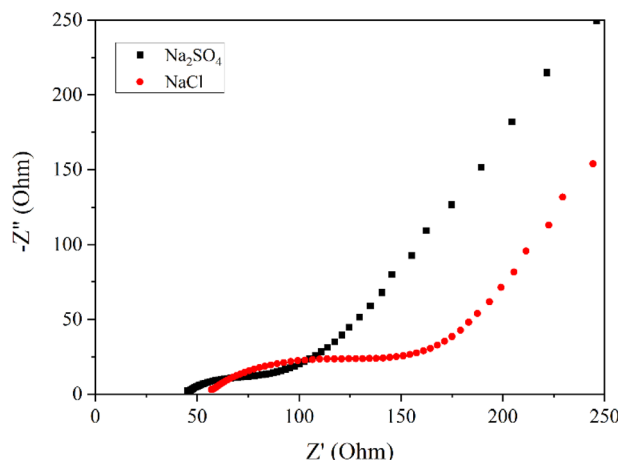


Fig. 3 Nyquist plots of  $\text{Mn}_3\text{O}_4$  thin film in  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ .

$\text{Na}_2\text{SO}_4$  electrolyte, presenting lower solution resistance and charge transfer resistance compared to  $\text{NaCl}$ . Additionally, the slope or inclination of the curve in the lower frequency region, indicating the Warburg impedance related to the ion diffusion process, suggests excellent capacitive behaviour in the  $\text{Na}_2\text{SO}_4$  electrolyte, despite the larger size of  $\text{SO}_4^{2-}$  ions compared to  $\text{Cl}^-$

ions. This trend may be ascribed to the higher concentration of  $\text{Na}^+$  ions in  $\text{Na}_2\text{SO}_4$  compared to  $\text{NaCl}$ . Upon dissociation,  $\text{Na}_2\text{SO}_4$  yields two  $\text{Na}^+$  ions and one  $\text{SO}_4^{2-}$  ion, whereas  $\text{NaCl}$  yields only one  $\text{Na}^+$  ion and one  $\text{Cl}^-$  ion. Given that these ions directly participate in redox reactions, the surplus of  $\text{Na}^+$  ions in  $\text{Na}_2\text{SO}_4$  provides more opportunities for adsorption and redox reactions. Consequently, the electrode in  $\text{Na}_2\text{SO}_4$  exhibits better storage behaviour compared to  $\text{NaCl}$ .

Furthermore, the GCD processes were investigated in  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  electrolytes at various current densities, as depicted in Fig. 4a–c shows the comparison at a particular current density. The linear relation between the charge/discharge potential and time indicates good capacitive behaviour.<sup>50</sup> The observed outcomes were found to be in good agreement with the findings obtained from CV and EIS analyses. The specific capacitance was derived from the GCD plot employing the following formula:

$$C = \frac{I\Delta t}{m\Delta V} \quad (5)$$

where  $I$  represent the discharge current,  $m$  indicates the mass of the deposited material,  $\Delta t$  signifies the discharge time, and  $\Delta V$  denotes the applied potential window. The highest specific capacitance attained was around  $131 \text{ F g}^{-1}$  for the  $\text{Na}_2\text{SO}_4$

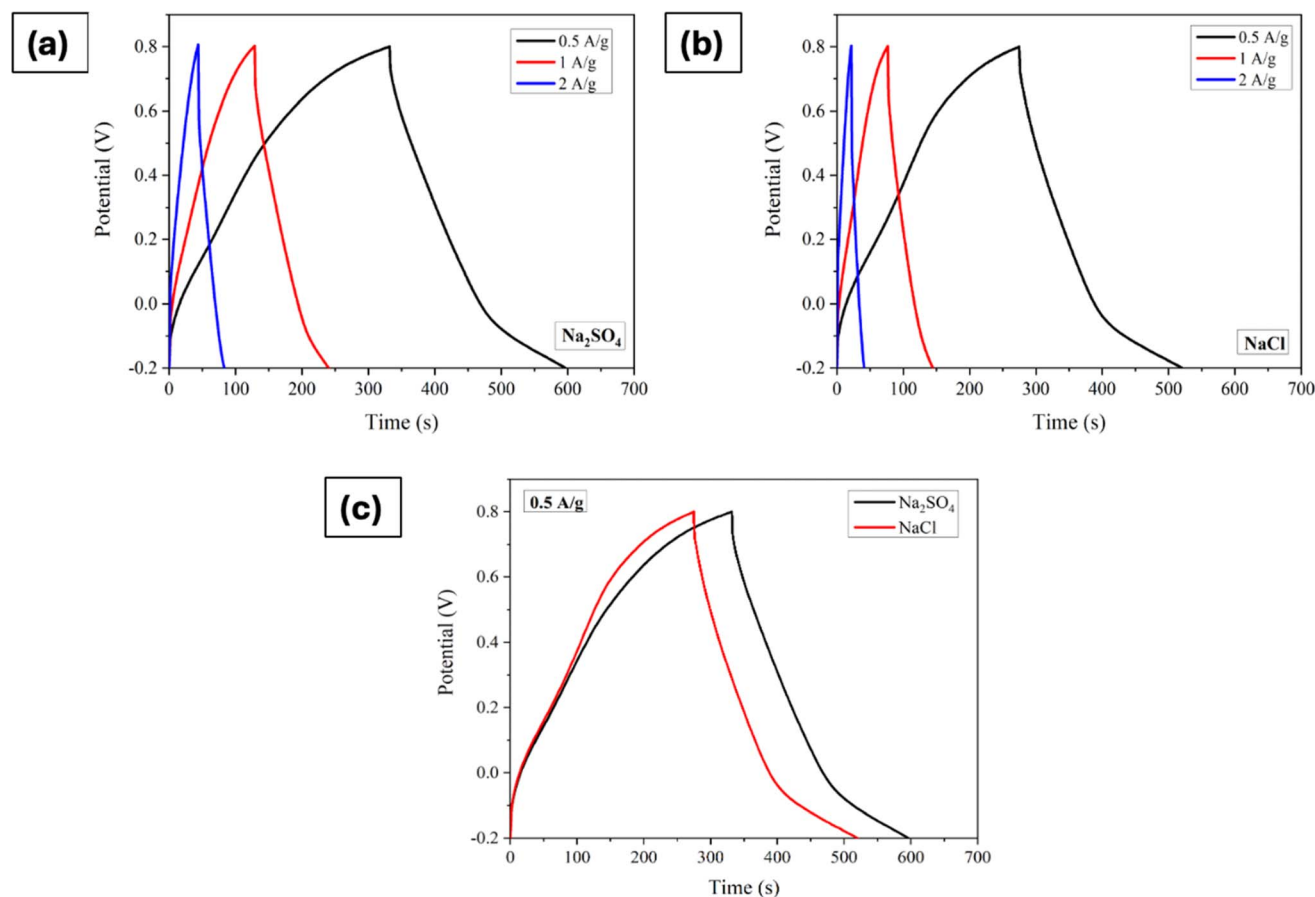


Fig. 4 Galvanostatic charge/discharge curves of  $\text{Mn}_3\text{O}_4$  thin film electrode in (a)  $\text{Na}_2\text{SO}_4$ , and (b)  $\text{NaCl}$ . (c) Comparison of GCDs at a current density of  $0.5 \text{ A g}^{-1}$ .



electrolyte, whereas a specific capacitance of  $122 \text{ F g}^{-1}$  was observed for the NaCl electrolyte.

Likewise, with anion fixed as sulphate ions, the influence of varying cations on electrochemical properties was investigated. Consequently,  $\text{Li}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{K}_2\text{SO}_4$  were employed as electrolytes, and Fig. 5a–d depicts the corresponding CVs obtained across a PW of  $-0.2 \text{ V}$  to  $0.8 \text{ V}$  at different scan rates. Consistently, similar to the findings across different anions, all electrodes displayed pseudocapacitive behaviour, with the current trending increased with scan rate. Upon closer examination at a scan rate of  $5 \text{ mV s}^{-1}$ , it becomes evident that  $\text{K}_2\text{SO}_4$  electrolyte yielded the highest curve area, indicative of superior capacitive behaviour, while  $\text{MgSO}_4$  exhibited the lowest. This disparity in curve areas hints at varying degrees of charge storage capability among the different cationic species.

Further analysis of specific capacitance values, calculated using eqn (4), revealed distinct trends. The values varied as  $94 \text{ F g}^{-1}$ ,  $112 \text{ F g}^{-1}$ ,  $132 \text{ F g}^{-1}$  and  $73 \text{ F g}^{-1}$  for  $\text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MgSO}_4$ , respectively. This order of specific capacitance ( $\text{K}^+ > \text{Li}^+ > \text{Na}^+ > \text{Mg}^{2+}$ ) can be rationalized by considering the ionic radii of these cations. Also, it is well known fact that, ions in the electrolyte are surrounded by water molecules, forming a hydration shell. The size of this hydration sphere impacts the ion's effective size. Larger hydration spheres can hinder ion

mobility, thus slowing the charge transfer process at the electrode surface. Specifically, the larger size of  $\text{K}^+$  ions enables easier diffusion and adsorption owing to their smaller hydration sphere radius.<sup>28,51,52</sup> Conversely, the lower specific capacitance observed in  $\text{MgSO}_4$  electrolytes may be attributed to the lower ionic size and higher hydration sphere radius of  $\text{Mg}^{2+}$  ions. However, an intriguing observation arises when comparing  $\text{Na}^+$  and  $\text{Li}^+$ . Despite  $\text{Na}^+$  offering better ionic conductivity and a smaller hydration sphere compared to  $\text{Li}^+$ ,  $\text{Li}_2\text{SO}_4$  demonstrated a higher specific capacitance. This discrepancy suggests that smaller size of  $\text{Li}^+$  may facilitate more favourable adsorption and desorption/intercalation processes. A comparable trend was seen for hydrothermally grown  $\text{Mn}_3\text{O}_4$  on carbon cloth.<sup>26</sup>

Fig. 6 presents Nyquist plots of the  $\text{Mn}_3\text{O}_4$  thin film electrode in various electrolytes, obtained from the EIS experiments. The electrodes in  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{Li}_2\text{SO}_4$  exhibit a similar capacitive trend with a vertical profile in the low-frequency region, indicating low diffusion resistance. Nevertheless, a significant deviation is witnessed in the inclination of the vertical line for the  $\text{MgSO}_4$  electrolyte, suggesting its high ionic resistance. This can be related to the lower mobility of  $\text{Mg}^{2+}$  ions due to their large hydration sphere radius.<sup>53</sup> Additionally, the high charge density of  $\text{Mg}^{2+}$  ions also results in strong

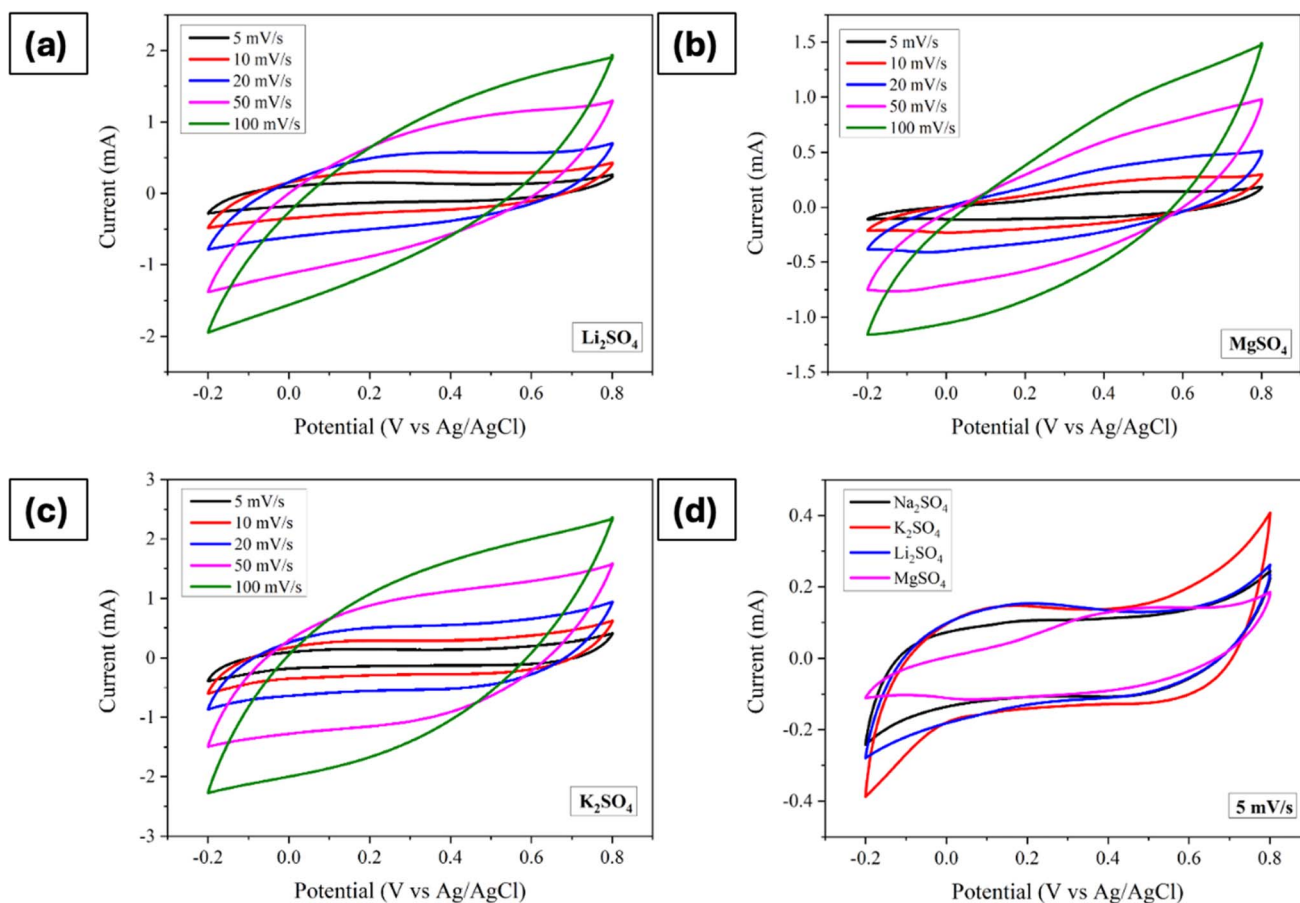


Fig. 5 Cyclic voltammograms of  $\text{Mn}_3\text{O}_4$  thin film electrode in (a)  $\text{Li}_2\text{SO}_4$ , (b)  $\text{MgSO}_4$ , (c)  $\text{K}_2\text{SO}_4$ , and (d) comparison of CVs at a scan rate of  $5 \text{ mV s}^{-1}$ .

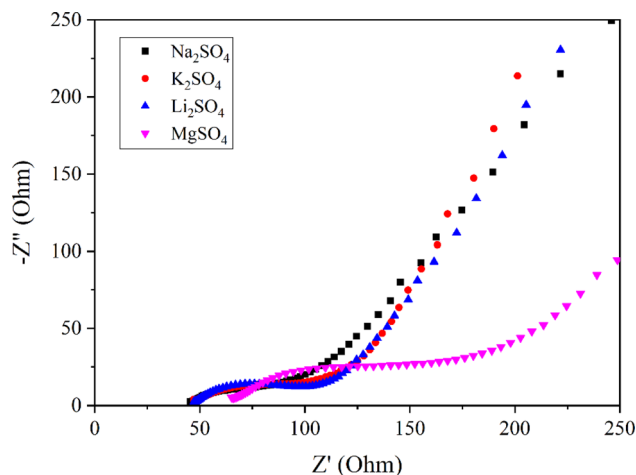


Fig. 6 Nyquist plots of  $\text{Mn}_3\text{O}_4$  thin film in electrolytes with different cations.

electrostatic interactions with surrounding electrolyte molecules, contributing to the high solution resistance and charge transfer resistance observed for  $\text{MgSO}_4$ .<sup>54</sup>

Fig. 7a–d displays the GCD curves of electrodes processed in electrolytes containing different cations with a comparison at

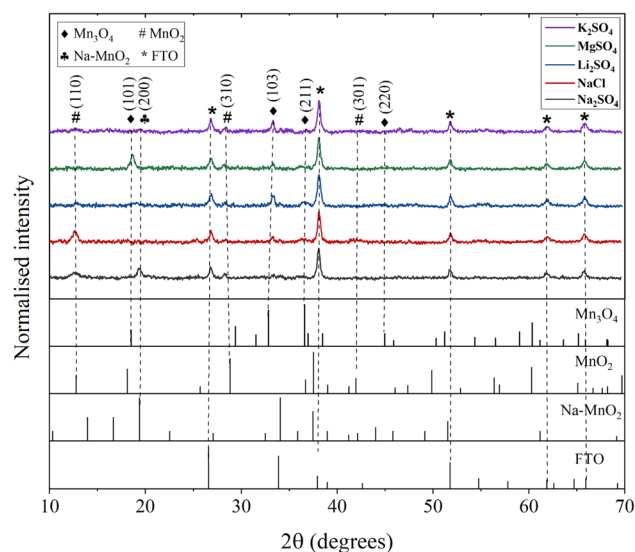


Fig. 8 XRD patterns of  $\text{Mn}_3\text{O}_4$  thin films after cycling in different electrolytes.

a current density of  $0.5 \text{ A g}^{-1}$ . The trends observed in the CV and EIS measurements are consistent here as well. Furthermore, it is apparent that the charge/discharge processes are linear with

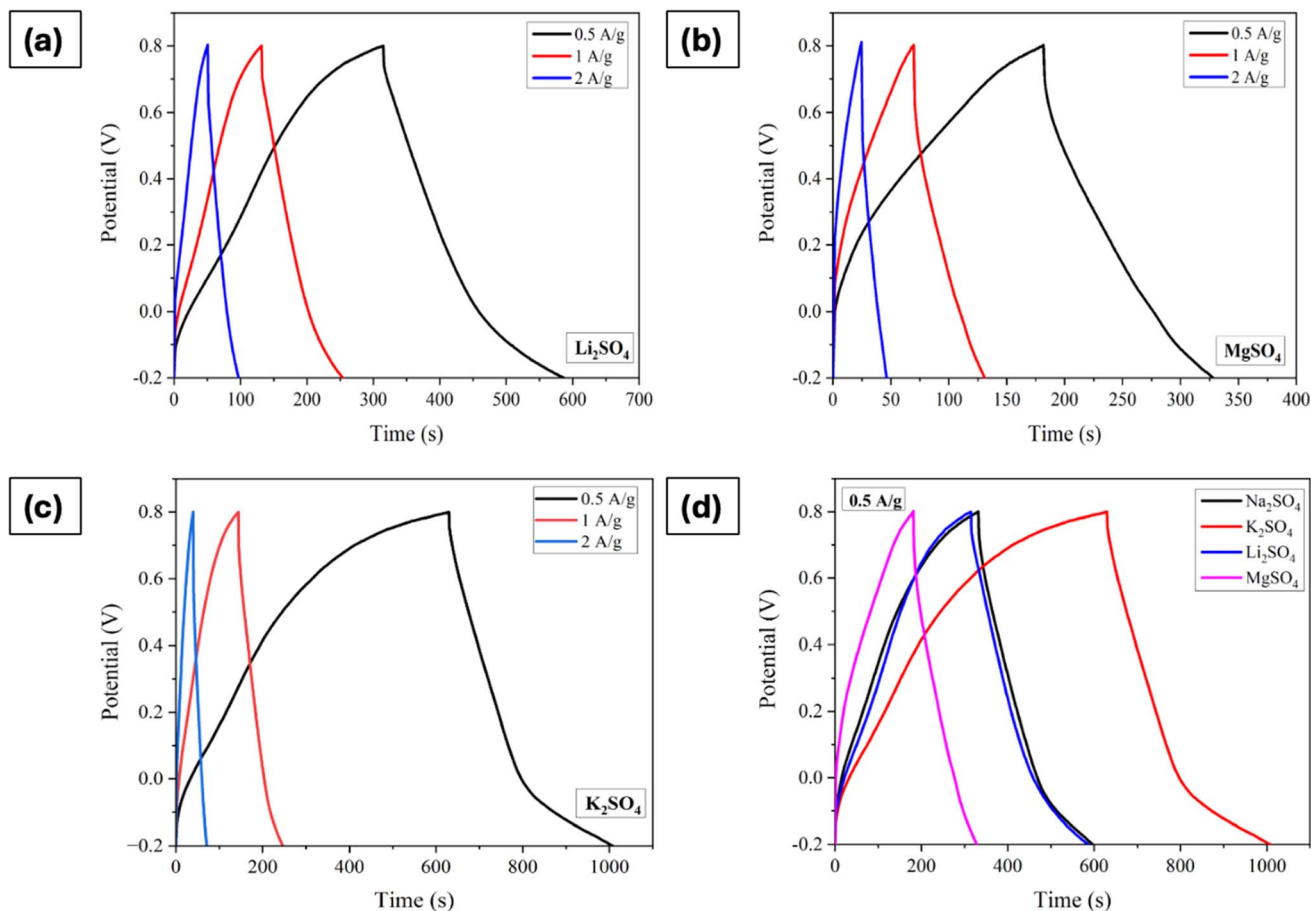


Fig. 7 GCD curves of  $\text{Mn}_3\text{O}_4$  thin film electrode in (a)  $\text{Li}_2\text{SO}_4$ , (b)  $\text{MgSO}_4$ , (c)  $\text{K}_2\text{SO}_4$ , and (d) comparison of GCDs at a current density of  $0.5 \text{ A g}^{-1}$ .



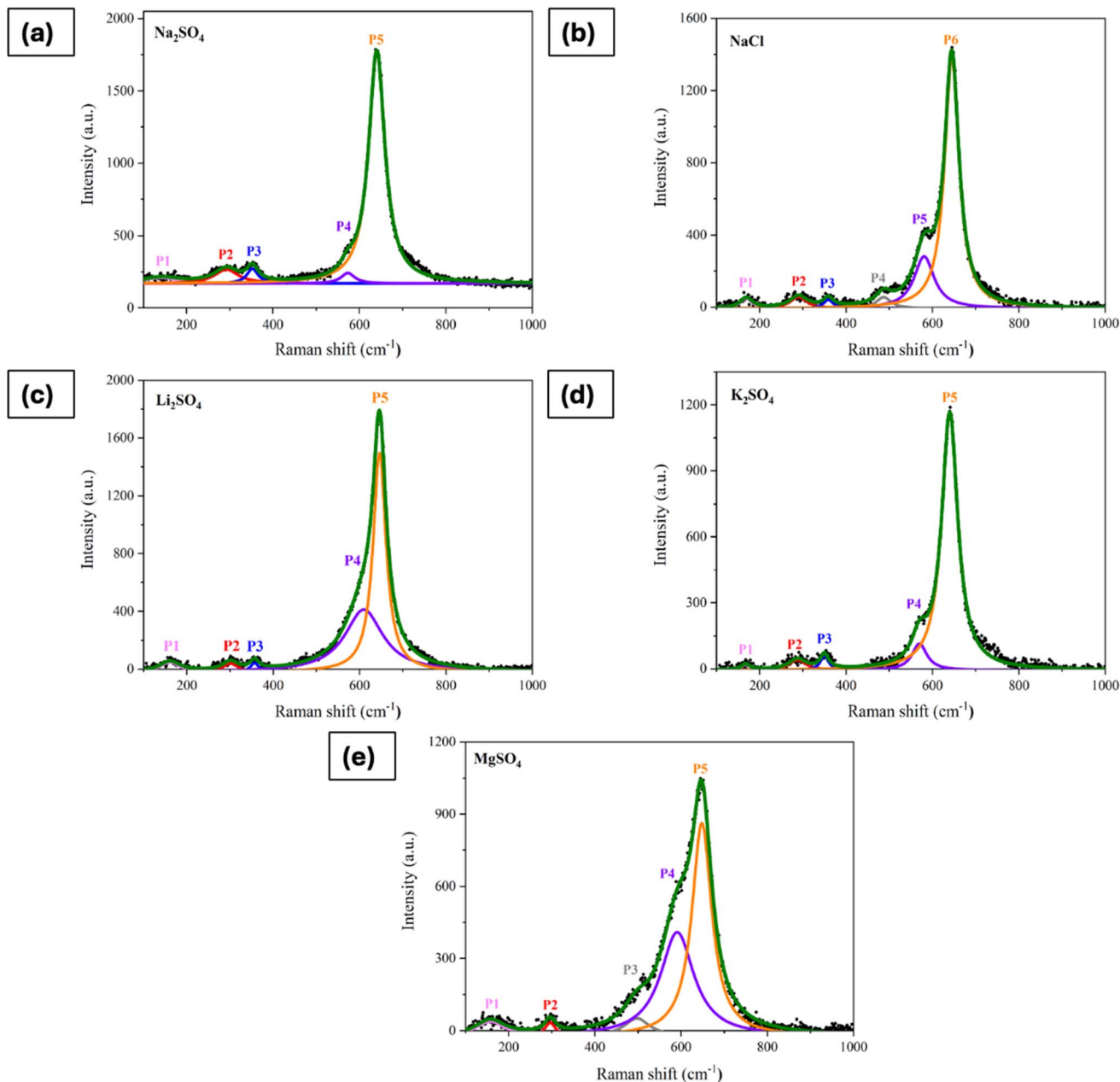


Fig. 9 Raman spectra of electrode processed in (a)  $\text{Na}_2\text{SO}_4$ , (b)  $\text{NaCl}$ , (c)  $\text{Li}_2\text{SO}_4$ , (d)  $\text{K}_2\text{SO}_4$ , and (e)  $\text{MgSO}_4$  for 500 CV cycles at  $50 \text{ mV s}^{-1}$ .

Table 1 Peak position in the Raman spectra of electrodes subjected to CV in different electrolytes

Mode	Peak position ( $\text{cm}^{-1}$ )					
	Before CV	$\text{Na}_2\text{SO}_4$	$\text{NaCl}$	$\text{Li}_2\text{SO}_4$	$\text{MgSO}_4$	$\text{K}_2\text{SO}_4$
Translational vibration of $\text{MnO}_6$ octahedra	—	141	168	161	157	167
$E_g$	310	292	290	300	296	287
$T_{2g}$ (2)	363	352	358	357	—	350
—	—	—	487	—	497	—
—	—	573	580	609	590	570
$A_g$	651	640	644	646	648	640





time irrespective of the cations. The specific capacitance values, determined using eqn (5), are  $131 \text{ F g}^{-1}$  for  $\text{Na}_2\text{SO}_4$ ,  $136 \text{ F g}^{-1}$  for  $\text{Li}_2\text{SO}_4$ ,  $187 \text{ F g}^{-1}$  for  $\text{K}_2\text{SO}_4$ , and  $96 \text{ F g}^{-1}$  for  $\text{MgSO}_4$  at  $0.5 \text{ A g}^{-1}$ .

### 3.3. Characterization of the electrodes after cycling

The electrode properties were further investigated post-cycling to assess the structural and morphological changes. The

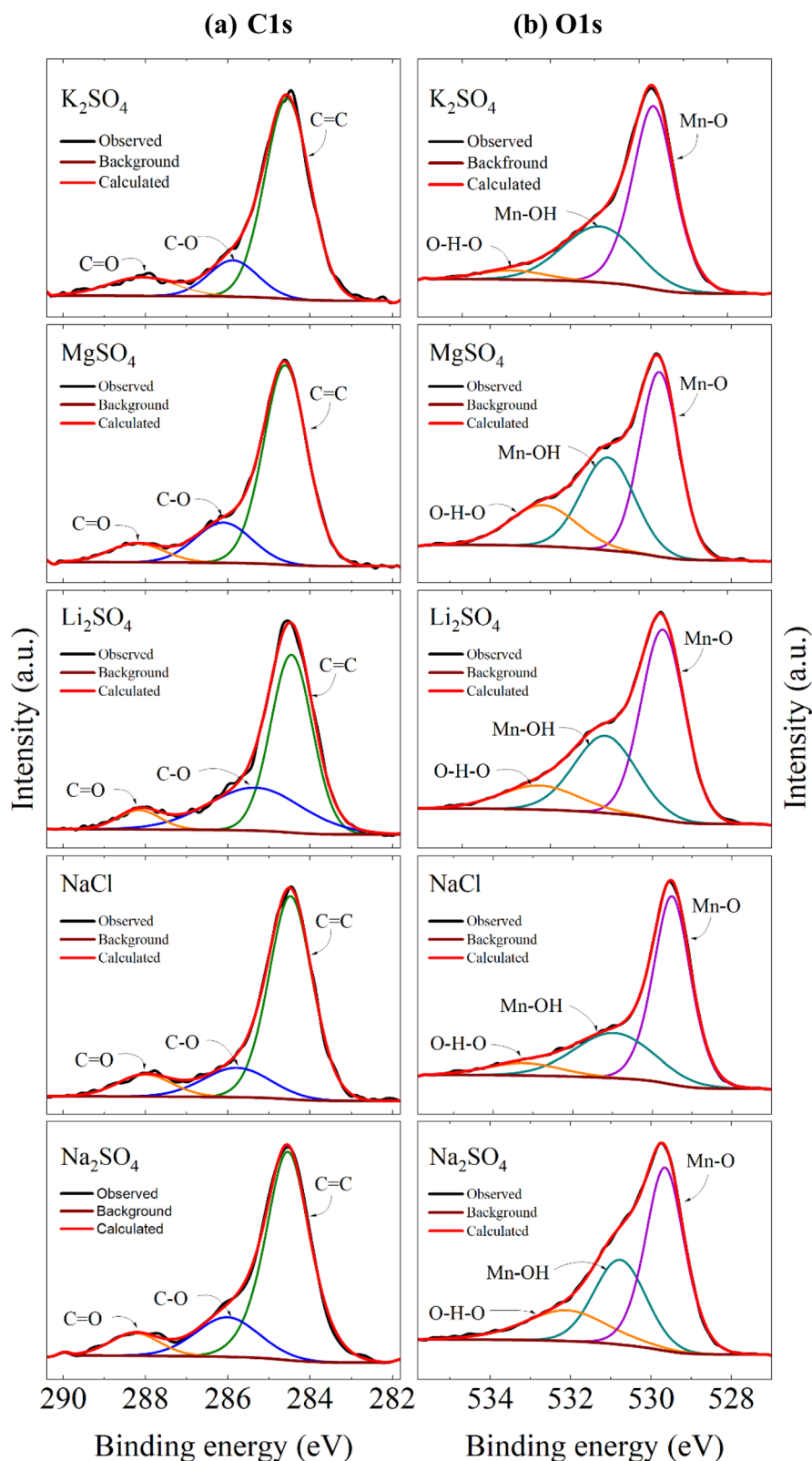


Fig. 10 Core level spectra of (a) C 1s and (b) O 1s for electrodes processed in different electrolytes.



electrodes were cycled for 500 CV cycles at a scan rate of 50 mV s<sup>-1</sup> and then subjected to various characterizations. Fig. 8 presents the XRD pattern of the electrodes after cycling in different electrolytes. As initially discussed with reference to Fig. 1, the electrode exhibited the Mn<sub>3</sub>O<sub>4</sub> phase before cycling. However, cycling induced changes in the electrode structure, evidenced by a decrease in the intensities of the Mn<sub>3</sub>O<sub>4</sub> planes. Additionally, new manganese oxide phases emerged, as reflected in the XRD patterns. For electrodes cycled in Na<sub>2</sub>SO<sub>4</sub> electrolyte, MnO<sub>2</sub>, and Na-MnO<sub>2</sub> (sodium birnessite) phases were detected, while in NaCl, only MnO<sub>2</sub> phases were observed. Previous literature has reported the conversion of Mn<sub>3</sub>O<sub>4</sub> to MnO<sub>2</sub> (termed as electrochemical activation) after certain CV and GCD cycles.<sup>25,55,56</sup> This phase transformation is due to the continuous redox reactions or intercalation/deintercalation of electrolyte ions within the spinel structure of Mn<sub>3</sub>O<sub>4</sub>.<sup>57</sup> According to the studies, this electrochemical activation will generally enhance the specific capacitance by creating new adsorption sites.<sup>58</sup> However, there was no complete phase transformation observed which might be due to the insufficient number of CV cycles.

To further validate the partial phase transformations, Raman spectra of the processed/activated electrodes were examined. Fig. 9a–e presents the deconvoluted Raman spectra of electrodes that underwent 500 CV cycles in various electrolytes, with the peak positions summarized in Table 1. Significant differences were seen in the activated electrodes when compared to the Raman spectra of the electrode prior to cycling (shown in Fig. S1†). Notably, there are intense peaks at 640–645 cm<sup>-1</sup>, along with peaks at around 490 cm<sup>-1</sup> and 580 cm<sup>-1</sup>, which are the features of vibrations in birnessite.<sup>27</sup> The vibrational mode in the lower wavenumber region (P1) is associated with the external vibration caused by the translational motion of MnO<sub>6</sub> octahedra.<sup>59</sup> Additionally, there were significant shifts in the E<sub>g</sub> and T<sub>2g</sub>(2) peaks, indicating variations in the Mn–O bending vibrations. These shifts are attributed to the formation of new phases during the electrochemical activation process.

XPS survey spectra of the electrodes cycled in different electrolytes are shown in Fig. S3.† The spectra reveal the presence of Mn 2p, O 1s along with C 1s in all the samples. In addition to that, as a consequence of cycling some of the peaks related to Na, K, and Mg also appeared in their respective spectra indicating the presence of surface adsorbed ions. Further, auger peaks of Mn and O have appeared in the spectra around the binding energy (BE) of 903.7 eV and 972.4 eV respectively.

Further, Fig. 10a shows the high-resolution C 1s spectra, which have been resolved into three peaks resembling with C=C, C–O, and C=O positioned in the ranges of 284.46–284.61 eV, 285.33–286.11 eV and 288.02–288.26 eV respectively after charge correction. Here the third component (C=O) in the higher binding energy appeared as a result of cycling. This peak was absent in the C 1s spectra of the electrode before cycling as shown in Fig. S2a.† These changes were also reflected in the O 1s core spectra as represented in Fig. 10b. The spectra have been deconvoluted into three peaks lying in the range of 529.46–529.79 eV, 530.76–531.07 eV, and 532.10–533.24 eV. The peak at

the lower binding energy features the lattice oxygen associated with the Mn–O covalent bond and the peak between 530.76–531.07 eV represents some surface adsorbed hydroxyl groups.

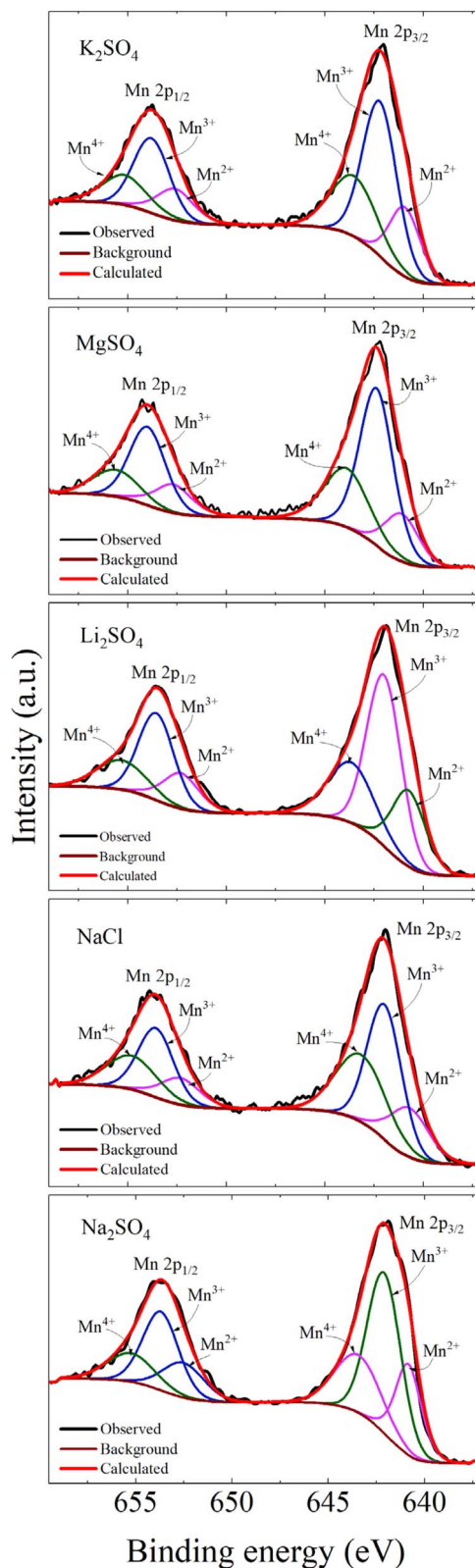


Fig. 11 Mn 2p core level spectra of the electrodes processed in different electrolytes.

The higher binding energy peak indicates the surface adsorbed water<sup>60</sup> or some carboxyl groups<sup>61</sup> as a result of continuous CV cycles. This intern supports the C=O component observed in C 1s spectra. However, this component was not observed in the electrode prior to the cycling (Fig. S2b†). The peak area under each component varies with the electrolyte used implying a variation of compositions with respect to the electrolytes.

The Mn 2p spectra as shown in Fig. 11 exhibit the spin-orbit coupling, resulting in two peaks, Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> with an

BE separation ranging from 11.69–11.79 eV for all the electrodes. In general, any energy separation greater than 11.05 eV (for metallic Mn) indicates the oxidative state of Mn.<sup>61</sup> Moreover, the BE difference between Mn 2p<sub>3/2</sub> and O 1s spectra (given in Table S1†) indicates an increment in the Mn<sup>4+</sup> state in the electrodes after cycling. It can be discerned that for the electrode before cycling the value of  $\Delta E(\text{Mn } 2p_{3/2}-\text{O } 1s)$  was 111.58 eV, which implies the electrode was rich in Mn<sup>2+</sup>. But electrochemical cycling resulted in a change in energy

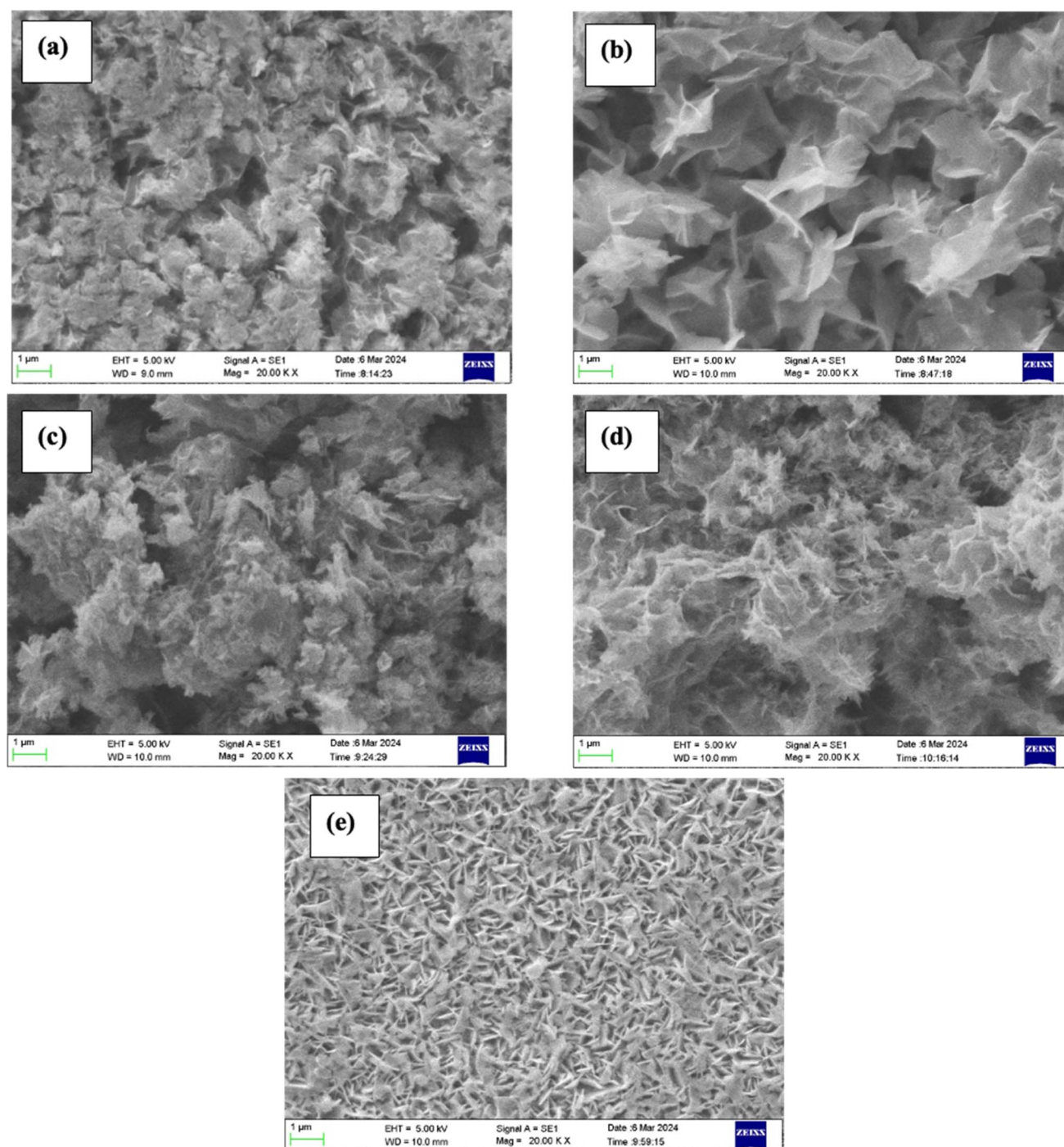


Fig. 12 SEM images of the electrodes processed in (a) Na<sub>2</sub>SO<sub>4</sub>, (b) NaCl, (c) Li<sub>2</sub>SO<sub>4</sub>, (d) K<sub>2</sub>SO<sub>4</sub>, and (e) MgSO<sub>4</sub> for 500 CV cycles at 50 mV s<sup>-1</sup>.





difference ranging from 112.31–112.5 eV, pointing out the evolution of the  $\text{Mn}^{4+}$  state.<sup>62</sup> These observations are in accordance with the XRD as well as Raman results where there was evidence of  $\text{MnO}_2$  phase as a consequence of cycling. Further, the Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  peaks are deconvoluted into three peaks each revealing the presence of  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  as well as  $\text{Mn}^{4+}$  states. The peak positions, FWHM, and area under each peak are tabulated in Table S1.<sup>†</sup> However, for the electrode before cycling, the presence of  $\text{Mn}^{4+}$  was evident (shown in Fig. S2c<sup>†</sup>), which was not the case for a pure  $\text{Mn}_3\text{O}_4$ . It is known that, for manganese oxide, surface cation defects are common along with oxygen defects.<sup>63</sup> Thus, the appearance of  $\text{Mn}^{4+}$  might be due to the cation vacancies.<sup>64</sup> Notably, for all the electrodes, after cycling there was an increase in the  $\text{Mn}^{4+}$  state and a decrease in the  $\text{Mn}^{2+}$  state, which suggests that cycling causes the oxidation of Mn thereby tending to form  $\text{MnO}_2$  as seen in XRD.

Fig. 12 displays the SEM images of electrodes activated in different electrolytes (Fig. S5<sup>†</sup> shows SEM images with different magnifications). It is evident from the figures that CV cycling significantly affected the surface of the electrodes which might be due to the phase transformation as seen in XRD and Raman studies. For the  $\text{Na}_2\text{SO}_4$ -activated electrode, the morphology

was changed from fibrous (before cycling) to a dense thin nanosheet-like structure whereas these nanosheets were more defined in the case of NaCl electrolyte. For  $\text{Li}_2\text{SO}_4$  the morphology was somewhat similar to that of  $\text{Na}_2\text{SO}_4$ . In case of  $\text{MgSO}_4$ , the nanosheets were more compact with lesser pore size whereas the  $\text{K}_2\text{SO}_4$ -activated electrode exhibited a very thin layer of nanosheets. These layered nanosheets indicate the formation of birnessite ( $\alpha\text{-MnO}_2$ ) as reported in the earlier report.<sup>27</sup>

Further, Fig. 13 shows the contact angle measurements of electrodes processed in different electrolytes for 500 CV cycles at  $50 \text{ mV s}^{-1}$ . Compared to the  $\text{Mn}_3\text{O}_4$  electrode before cycling (as shown in Fig. 3c), all the electrodes exhibit very good wettability, where there was a significant decrease in the contact angle. The hydrophilicity of the electrodes was improved and the electrode processed in  $\text{K}_2\text{SO}_4$  electrolyte was found to be highly hydrophilic. This can be witnessed from the SEM image of the  $\text{K}_2\text{SO}_4$  processed electrode where there are very thin layered structures. This further implies that the  $\text{K}_2\text{SO}_4$  processed electrode has higher surface energy and surface area compared to other electrodes.<sup>65</sup> On the other hand,  $\text{MgSO}_4$  processed electrode has high contact angle which might be due to its lesser surface area and surface roughness. However, surface wettability was

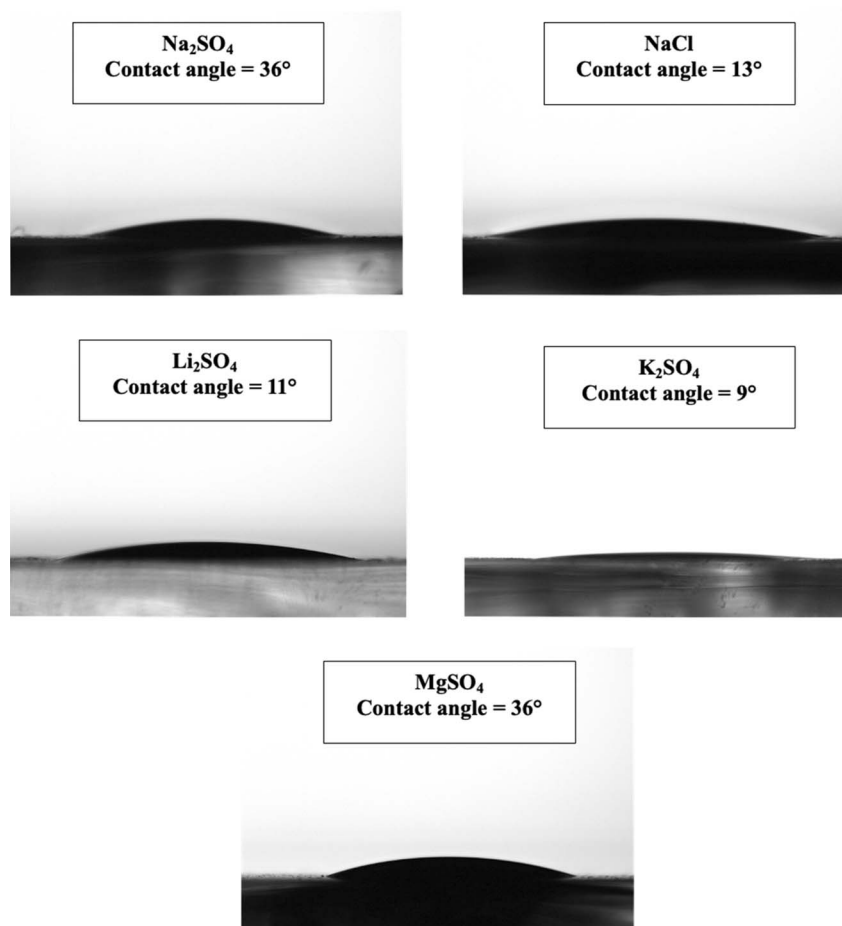


Fig. 13 Contact angle measurements of the electrodes processed in (a)  $\text{Na}_2\text{SO}_4$ , (b) NaCl, (c)  $\text{Li}_2\text{SO}_4$ , (d)  $\text{K}_2\text{SO}_4$  and (e)  $\text{MgSO}_4$  for 500 CV cycles at  $50 \text{ mV s}^{-1}$ .

**Table 2** Areal capacitance of the electrode calculated at 1st and 500th cycle

Electrolyte	Areal capacitance (mF cm <sup>-2</sup> )		
	1st cycle	500th cycle	Increment (times)
Na <sub>2</sub> SO <sub>4</sub>	28.34	37.48	1.3
NaCl	22.20	35.52	1.6
Li <sub>2</sub> SO <sub>4</sub>	29.40	40.66	1.4
MgSO <sub>4</sub>	19.95	36.60	1.8
K <sub>2</sub> SO <sub>4</sub>	33.12	42.94	1.3

significantly improved after cycling which indicates better storage performance.

**3.3.1 Electrode performance after cycling.** To see the changes in the storage performance after 500 CV cycles, cyclic voltammograms were collected for each electrode. Fig. S6† shows the comparison between the 1st and 500th cycles and the calculated areal capacitance is tabulated in Table 2. It has been perceived that the storage performance of all the electrodes improved after cycling which might be due to phase transformation as seen earlier. This type of phase transformation after cycling which enhances the specific capacitance is termed electrochemical activation.<sup>58</sup> However, in this case, there is no complete phase transformation of Mn<sub>3</sub>O<sub>4</sub> to MnO<sub>2</sub> during 500 cycles. The increment in the specific capacitance may be accredited to the modification in the morphology and thus the surface roughness. This may induce new adsorption sites for more reactions to occur. Notably, when comparing with different electrolytes, the electrode in MgSO<sub>4</sub> showed good storage performance with cycling, even though it has poor specific capacitance. Compared to the first cycles, the capacitance improved up to 1.8 times for the MgSO<sub>4</sub> processed electrode after 500 cycles. This can be explained on the basis of XPS where for the MgSO<sub>4</sub> processed electrode there was more amount of Mn in higher oxidation states (high Mn<sup>3+</sup>/Mn<sup>2+</sup> ratio and low Mn<sup>2+</sup>/Mn<sup>4+</sup> ratio). On the other hand, with cycling more Mn<sup>2+</sup> ions are getting oxidised into Mn<sup>3+</sup> and Mn<sup>4+</sup> in MgSO<sub>4</sub>. This in turn suggests that the efficiency for electrochemical activation is higher in MgSO<sub>4</sub> than in other electrolytes.

## 4. Conclusions

In summary, the Mn<sub>3</sub>O<sub>4</sub> thin film electrodes were synthesised using the chemical spray pyrolysis technique, and its electrochemical properties in different aqueous electrolytes were examined. The as-synthesized electrode is crystalized in a tetragonal crystal structure and the observed Raman modes are agreeing with the spinel Mn<sub>3</sub>O<sub>4</sub>. Electrochemical testing in electrolytes with dissimilar anions and cations revealed the consequences of ion size and hydration sphere radius on the charge storage kinetics. Accordingly, the electrode processed in K<sub>2</sub>SO<sub>4</sub> electrolytes exhibited the highest specific capacitance of around 187 F g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup>. Moreover, post-cycling structural studies implied that there was a partial phase transformation of the electrodes from Mn<sub>3</sub>O<sub>4</sub> to MnO<sub>2</sub>

phase after 500 CV cycles. Consequently, XPS results support this by showing higher oxidation states of Mn. Also, the electrochemical cycling significantly altered the morphology from fibrous to layered, whereas the wettability of the electrodes was also improved accordingly. A comparison of capacitance between the first and 500th cycle illustrate that, the electrode processed in MgSO<sub>4</sub> electrolyte has more tendency to undergo oxidation with cycling as evidenced by its capacitance value which improved 1.8 times of its initial capacitance. The results outlined here thus help to access the influence of cations and anions on the electrochemical performance of Mn<sub>3</sub>O<sub>4</sub> thin films in aqueous electrolytes, thereby pointing their suitability for supercapacitor application.

## Data availability

Data can be made available on a reasonable request to the corresponding author. The most data pertaining to this article is mentioned in the article itself. Additionally, the data supporting this article have been included as part of the ESI.†

## Author contributions

Pramitha A: conceptualization, investigation, formal analysis, writing – original draft. Shreeganesh Subraya Hegde: validation, writing – review & editing. Badekai Ramachandra Bhat: validation, resources, writing – review & editing. Sajan D. George: validation, resources. Raviprakash Y: conceptualization, visualization, validation, writing – review & editing, resources, supervision.

## Conflicts of interest

There are no conflicts to declare.

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