Supporting Information

Triple Perovskite oxide as an Advanced Pseudocapacitive Material: Multifarious Element Approach with Ordered Structure

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1. Synthesis of Triple perovskite oxides

Sol-gel method is adopted to synthesize triple perovskite $Sr_3CoFeMoO_{9-\delta}$ (SCFM). Typically, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were taken in a respective molar ratio and dissolved in aqueous solution (25 mL) of oxalic acid. The metal ions/oxalic acid ratio was maintained as 1:1. This solution was stirred vigorously for 3 hr at 90 °C to obtain a viscous gel. The calcination of formed gel for 4 hr at 400 °C then with further increase in temperature to 600 °C for duration of 2 hr ensured complete removal of the organic moieties. Finally, the sample was cooled to room temperature and then the grounded sample is heated at 1000 °C for 10 hr. For comparison, other triple perovskites such as $Sr_3NiFeMoO_{9-\delta}$ and $Sr_3MnFeMoO_{9-\delta}$ were also synthesized by the same route.

2. Calculations

Specific capacitance ($C, F g^{-1}$) of working electrodes was evaluated from the CV curves using the given equation:¹

$$C = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} |i| dV$$
 S1

where *m* is the mass of the active material on electrode (g), *v* is the scan rate (V s⁻¹), V_a represents initial voltage (V) while V_c represents final voltage (V), and *i* is the current density (A cm⁻²).

Specific capacitance (C_{sp} , Fg_{-1}) and specific capacity (C_s , mAh g^{-1}) of working electrodes were evaluated from the GCD curves using the given equation:

$$C_{sp} = \frac{\frac{2i}{m\int V dt}}{V_{max}^2}$$
 S2

$$C_S = \frac{C_{sp} \times V_{max}}{3.6}$$
 S3

Where, C (F g⁻¹) represent galvanostatic charge/discharge specific capacitance, ${}^{i}m$ is the current density I/m (A g⁻¹), I is the current, m is active mass of electrode, $\int V dt$ is the integral area under the discharge curve, V_{max} is the maximum potential excluding IR-drop (V) [1]. The double layer capacitance (C_{dl}) and electrochemical accessible surface area (S_E) were determined using following equations;

$$|\Delta J| = (J_a - J_c) = C_{dl} \times \text{scan rate}$$
 S4

where, ΔJ is the current density, $J_a \& J_c$ is the current density at anode and cathode respectively, C_{dl} is the double layer capacitance (F g⁻¹). The obtained C_{dl} value from slope was divided by 20 μ F cm⁻² to calculate S_E [2].

To determine the mechanism behind charge storage power's law is implied using equation:³

$$i(V) = a\vartheta^b$$
 S5

Here, *a*, and *b* are adjustable parameters and *v* is the scan rate (V s⁻¹).

The following equation determines the contribution of current from capacitive and intercalation mechanism [3].

$$i(V) = k_1(\vartheta) + k_2(\vartheta)^{\frac{1}{2}}$$
 Set

The value of $k_1(v)$ and $k_2(v)^{1/2}$ gives the current contribution from capacitive and diffusion controlled intercalation mechanism respectively.

The specific capacitance (C_m , F g⁻¹), specific capacity (C_s , mAh g⁻¹), energy density (E, $Wh Kg^{-1}$) and power density (P, WKg^{-1}) of symmetric supercapacitor cell from the GCD curves were deduced according to the following equations:

$$C_{m} = \frac{\frac{2i}{m \int V \, dt}}{V_{max}^2}$$
 S7

$$C_S = \frac{C_{sp} \times V_{max}}{3.6}$$
 S8

$$E = \frac{I \int V \, dt}{M}$$
 S9

$$P = \frac{E \times 3600}{\Delta t}$$
 S10

where, C_m is the specific capacitance (F g⁻¹), i_m is the current density I/M (A g⁻¹), I is the current, M is total active mass of electrodes, $\int V dt$ is the integral area under the discharge curve, V_{max} is the maximum potential excluding IR-drop (V), Δt is the discharge time. [1] The oxygen vacancy concentration from the TGA results can be evaluated using equation given below [4]:

$$\delta = \frac{M}{16} \left(\Delta W_{N_2} \% - \Delta W_{air} \% \right)$$

where, δ is the oxygen vacancy concentration variation, M is Molecular weight, ${}^{\Delta W_{N_2}\%}$ and $\Delta W_{air}\%$ are the weight change percentage of SCFM in N₂ and air atmosphere.

Calculation of charge storage for asymmetric cell at positive and negative electrode is done using equation: [5]

$$q(C) = C_{sp} \times \Delta V \times m$$
^{S12}

Balancing of charge by substitution of above equation on considering charge/mass ratio, following equation is used with total mass loading of 1.4 mg:

$$\frac{q_{+}}{q_{-}} = \frac{m_{+}}{m_{-}} = \frac{C_{sp} - \Delta V_{-}}{C_{sp} + \Delta V_{+}}$$

S13

3. Material Characterization

For study of structural attributes, X-ray diffraction patterns were recorded (2 to 80°) using XRD BRUKER D8 advance with Cu kα 1.54 Å. The chemical states were identified by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA 165 with C 1s peak at 284.8 eV used as standard). The surface composition was estimated by Thermo Gravimetric Analysis (LINSEIS for air and PERKIN-ELMER. Morphological and defect studies were carried out by High resolution transmission electron microscopy (HRTEM, Phillips Technai T-300 microscope) and scanning electron microscope (SEM, ZEISS GEMINI). Inductively Coupled Plasma Mass Spectrometry (Agilent's 7900 ICP-MS) was employed to detect cations in electrolyte solution.

4. Electrochemical measurements and cell fabrication

All the electrochemical measurements including cyclic voltammetry (CV), Linear sweep voltammetry (LSV), Electrochemical Impedance analysis (EIS), chronoamperometry and galvanostatic charge discharge (GCD) are carried out using CHI 760C workstation. The working

electrodes were fabricated onto graphite sheet using the dispersion of 20 mg sample (80% active material, 15% AC black with 5 % PVDF binder) in isopropyl alcohol (IPA). The three electrode electrochemical studies are performed using 6M KOH with Ag/AgCl as the reference and a platinum plate (0.25 mm of thickness) as counter electrode. Further aqueous symmetric cell were fabricated by sandwiching triple material electrodes using separating membrane (Glass microfiber filters). The fabricated symmetric cell was taken in a glass vial and dipped in aqueous electrolyte up to 1 cm⁻² area before taking any electrochemical measurements. The mass loading ~ 0.6 mg cm⁻² is used during all electrochemical measurements.

Table S1: Atomic Percentage of Sr₃CoFeMoO_{9-δ} from XPS and EDAX.

Atomic	Sr	Со	Мо	Fe	0
Percentage (%)					
XPS	14.99	4.88	4.71	4.28	71.14
EDAX	14.69	3.88	5.30	4.29	71.84



Fig. S1. EDAX spectrum of Sr₃CoFeMoO_{9-δ}.



Fig. S2. Cyclic voltammetry responses of SCFM in different potential windows (a) -1 to -0.2 V,



Fig. S3. Galvanostatic charge discharge measurements at different current densities in different potential windows. (a) -1 to -0.2 V, (b) -0.2 to 0.4 V. (c) Variation of specific capacitance with current densities obtained in different windows region.



Fig. S4. BET isotherm of SCFM. Inset shows the BJH pore size distribution.

 Table S2: ICP-MS results of electrolyte after 5000 cycles.

Element	Sr	Со	Fe	Мо
Leaching (mg L ⁻¹)	0.110	0.038	0.451	0.837



Fig. S5. SEM micrograph of SCFM electrode after 10,000 cycles.



Fig. S6. Charge/discharge curve comparing graphite with SCFM.



Fig. S7. LSV measurement of graphite and SCFM in negative and positive potential region.



Fig. S8. Digital photograph of graphite electrode at the (a) negative potential window of -2V, (b) positive potential window of 2V, and (c) current potential window (-1 to 0.4V) after 5000 cycles.



Fig. S9. Graphite electrode (a) before cycling, and (b) after 5000 GCD cycling within the potential window of -1.0 V to 0.4 V.



Fig. S10. CV curves of SCFM SCFM SCFM cell at high scan rate region.



Fig. S11. Electrochemical performance of Activated carbon. (a) Voltammetric responses at different scan rate in -1 to 0 V window. (b) Oxygen evolution occurs above 0.4 V. (c) Galvanostatic charge discharge at different current densities.

The electrochemical performance of AC is evaluated at both positive and negative regions. At negative region, it exhibits larger potential window (-1–0V) than positive region where oxygen evolution is seen to occur after 0.4V (Fig. S11a & b). Charge/discharge measurement also shows considerable charge storage (Fig. S11c).



Fig. S12. Galvanostatic charge discharge profile of SCFM AC asymmetric cell at different current density.

The constructed asymmetric cell SCFM $\|$ AC (Fig. S12) shows a maximum capacitance of 155.7 F g⁻¹ and 25.77 F g⁻¹@20 A g⁻¹ which is about half of integrated supercapacitor cell SCFM $\|$ SCFM (56.96 F g⁻¹@20 A g⁻¹).



Fig. S13. Cycling stability test of SCFM SCFM SCFM cell.

The cycling stability of SCFM SCFM SCFM cell is evaluated and upto certain cycles activation occurs with retention of 125% after 10000 cycles (Fig. S13). The charge/discharge curve at different cycles shows the transition in discharge time from 100th cycle to 10000th cycle (inset Fig. S13).



Fig. S14. X-ray diffraction pattern of Sr₃NiFeMoO_{9-δ}.





Fig. S15. SEM micrograph and mapping of elements present in Sr₃NiFeMoO_{9-δ}.

Fig. S16. Electrochemical performance of $Sr_3NiFeMoO_{9-\delta}$. (a) Voltammetric responses at different scan rate in -1 to 0.5 V window. (b) CV curves of $Sr_3NiFeMoO_{9-\delta} \parallel Sr_3NiFeMoO_{9-\delta}$ cell at different scan rate. (c) Galvanostatic charge discharge (GCD) at different current densities. (d) Ragone plot.

Electrochemical performance of $Sr_3NiFeMoO_{9-\delta}$ is analysed first in three electrode set up that shows wide potential window covering positive and negative potential region (Fig. S16a). Further, the ability as an integrated supercapacitor is evaluated through CV (Fig. S16b) and GCD measurements (Fig. S16b) that shows a significant charge storage performance (245.85 F g⁻

¹@2.5 A g⁻¹). The maximum energy density is found to be 72.78 Wh kg⁻¹@1447.553 W kg⁻¹ (Fig. S16d).



Fig. S17. Voltammetry response of $Sr_3NiFeMoO_{9-\delta}$ electrode before and after 50 cycles.

After 50 cycles, $Sr_3NiFeMoO_{9-\delta}$ shows a significant increment in peak current like battery materials that restrict its further exploration (Fig. S17).



Fig. S18. X-ray diffraction pattern of Sr₃MnFeMoO_{9-δ}.



Fig. S19. SEM micrograph and mapping of elements present in Sr₃MnFeMoO_{9-δ}.



Fig. S20. Electrochemical performance of $Sr_3MnFeMoO_{9-\delta}$. (a) Voltammetric responses at different scan rate in -1 to 0.4 V window. (b) CV curves of $Sr_3MnFeMoO_{9-\delta}$ || $Sr_3MnFeMoO_{9-\delta}$ cell at different scan rate. (c) Galvanostatic charge discharge at different current densities. (d) Ragone plot.

The ability of $Sr_3MnFeMoO_{9-\delta}$ as an integrated electrode is analysed and it displays wide potential window covering positive and negative potential region (Fig. S20a). Further, as an integrated supercapacitor, CV measurements show a limited potential upto 1.3 V (Fig. S20b). Further, GCD measurements (Fig. S20b) show a substantial charge storage performance (172.6 F $g^{-1}@2.5 A g^{-1}$). The maximum energy density is found to be 38.24 Wh kg⁻¹@1229.14 W kg⁻¹ (Fig. S20d).

References

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