

Electronic Supporting Information (ESI) for:

Advanced Perspective on Synchronized Bifunctional Activities of P2-Type Material to Implement Interconnected Voltage Profile for Seawater Battery

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1. Rotating disk electrode measurements:

Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) were carried out on same rotating disc electrode and same setup. However, OER was carried out without rotation and ORR with different rotation speed. For the significant OER and ORR activity measurements, the cathode ink contains 5 mg of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst, 100 μl 5 wt% of Nafion solution, 200 μl ethanol and 600 μl water (1:3 ratio for water and ethanol) was prepared by 1 h sonication to obtain homogeneous suspension. Consequently, the cathode ink (3 μl contains $\sim 16 \mu\text{g}$) was loaded onto a surface of glassy carbon rotating disk electrode (3 mm diameter, loading $\sim 0.23 \text{ mg cm}^{-2}$) and dried for further respective linear sweep voltammetry (LSV) and cyclic voltammetry (CV) studies by VMP3 Biologic instrument. The OER and ORR activity measurements were carried out using three electrode setup and corresponding to glassy carbon rotating disk electrode used as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode in seawater or 0.1 M KOH aqueous electrolyte. In addition to this, the similar OER and ORR studies were carried out to IrO_2 and 20% Pt/C catalysts (Alfa aesar) for the standard, representing OER and ORR catalysts. The LSV studies for OER catalytic activity of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst were investigated in comparison with IrO_2 catalyst in seawater and 0.1 M KOH aqueous electrolyte at 5 mV s^{-1} . Subsequently, cathodic polarization LSV curves for the ORR characteristic of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst and 20% Pt/C catalyst were measured in O_2 saturated condition at different rotation speed 400 to 2225 rpm with the scan rate of 5 mV s^{-1} in seawater and 0.1 M KOH aqueous electrolyte. Finally, CV analysis were used to confirm the ORR catalytic activity in N_2 and O_2 saturated condition for P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst and 20% Pt/C catalyst using seawater and 0.1 M KOH aqueous electrolyte between 0.4 to -0.7 V at 5 mV s^{-1} .

2. Assembling of seawater battery:

Seawater battery is having two compartments such as non-aqueous 1 M NaCF_3SO_3 in TEGDME electrolyte and aqueous seawater catholyte. Initially, the non-aqueous compartment, having sodium metal or hard carbon as an anode (16 mm diameter), was assembled in an argon-filled glove box (KIYON) with the configuration of coin type cell using 1 M NaCF_3SO_3 in TEGDME electrolyte and celgard separator for half-cell and full-cell seawater batteries. The celgard

separator was used to prevent any unwanted chemical reaction between anode and pelletized ceramic NASICON solid electrolyte in non-aqueous anode compartment. Therefore, the aqueous compartment was contained a cathode into seawater catholyte with titanium current collector. For the fabrication of seawater battery cathode, the slurry contains 80% active material, 10% SP-carbon (Timcal) and 10% poly(vinylidene fluoride) in N-methyl-2-pyrrolidone, loaded on heat treated carbon felt (500 °C for 4 h, 16 mm diameter) and dried at 80 °C in vacuum oven. Finally, seawater battery was assembled using fabricated non-aqueous and aqueous compartments with the continuous seawater catholyte circulation by electric motor pump.

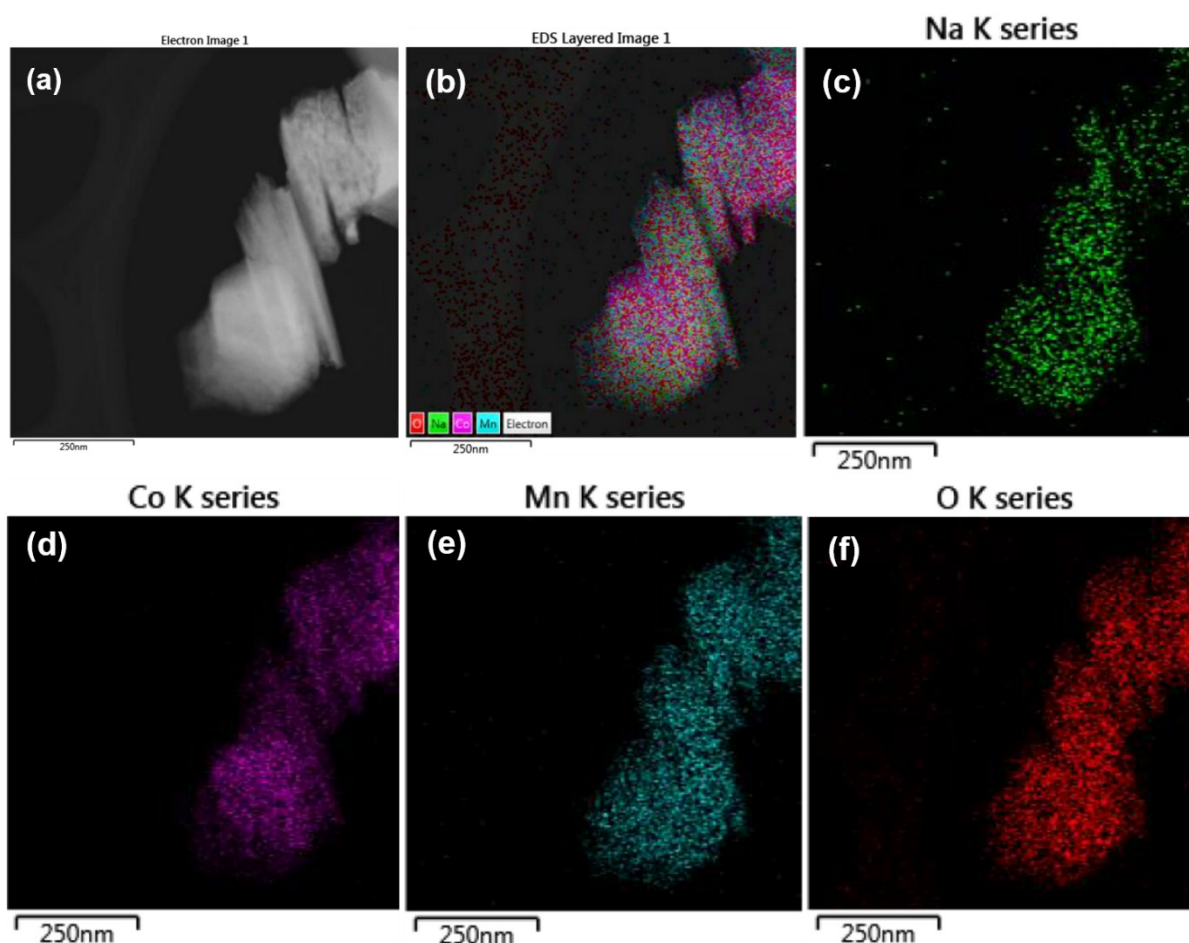


Fig. S1 Morphology and elemental mapping studies: (a) high-resolution transmission electron microscopy image of the P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst revealed flaky-bundle morphology with the flaky size of ~ 30 nm; (b) elemental mapping related presence of Na, Co, Mn and O; (c) Na in green; (d) Co in purple; (e) Mn in dark cyan and (f) O in red for the P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst.

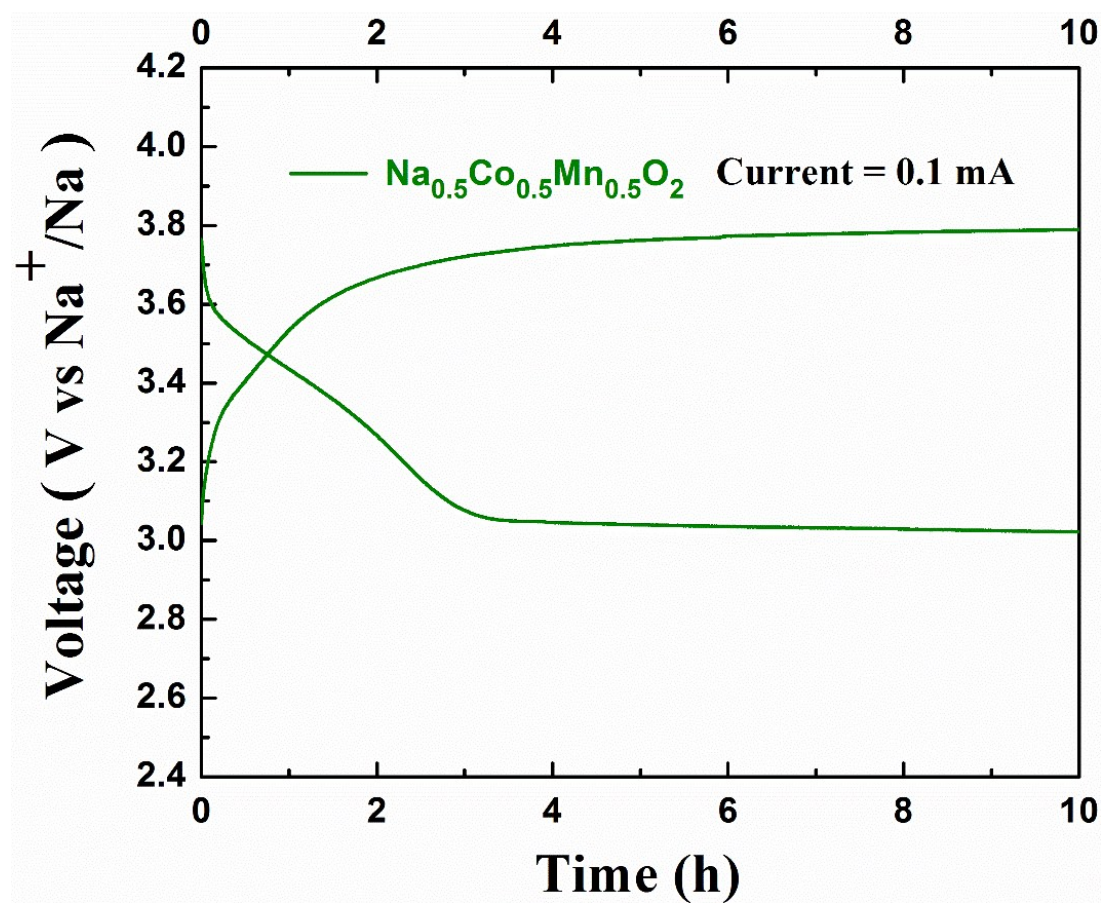


Fig. S2 Apparent OER and ORR characteristics with an intercalation-deintercalation characteristics of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst: voltage vs time performance for half-cell seawater batteries (Na vs P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst) corresponding to charge-discharge cycling at 0.1 mA for 10 h using non-aqueous (1 M NaCF_3SO_3 in tetraethylene glycol dimethyl ether) and aqueous seawater electrolyte (catholyte).

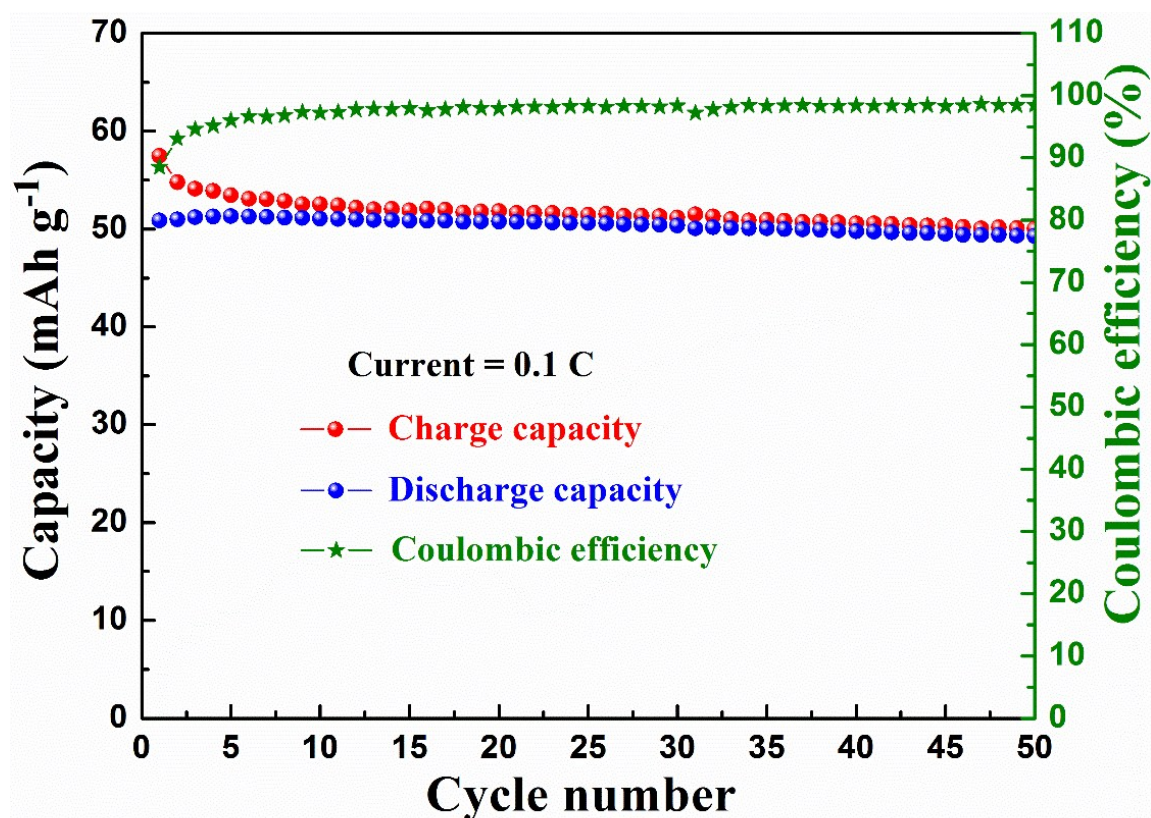


Fig. S3 Na-ion half-cell cycling performance of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst: capacity vs cycle number performance of fabricated coin type Na-ion half-cell (Na vs P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst) cycled in between 3.0 to 4.4 V at 0.1 C for 50 cycles using non-aqueous 1 M NaPF_6 in 1:1 (v/v) EC-PC with FEC (5% wt.) additive electrolyte.

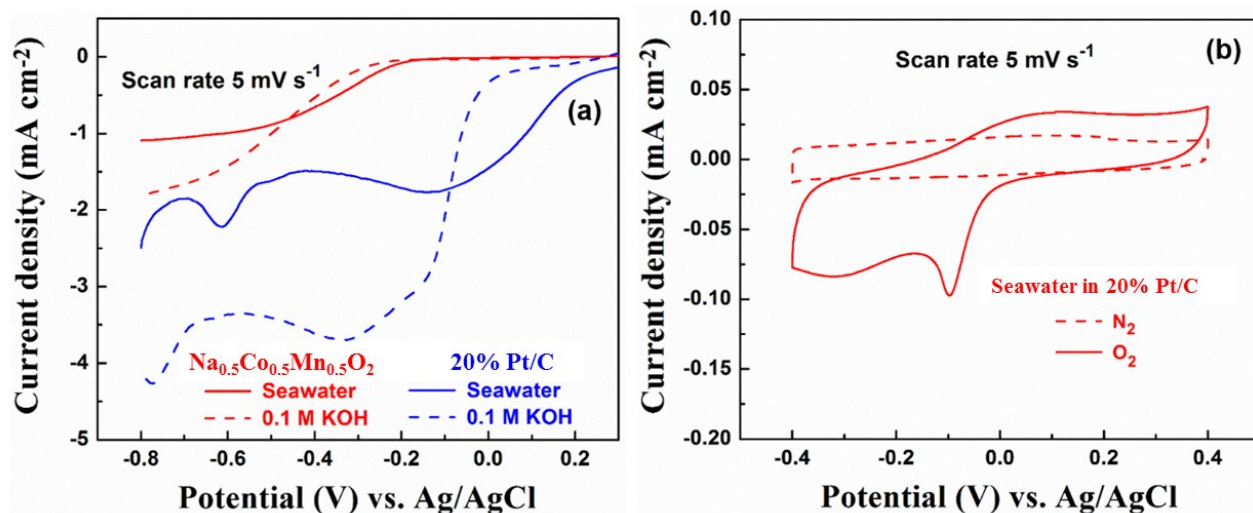


Fig. S4 Catalytic studies of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst: (a) cathodic polarization curves comparison of P2-type layered $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrocatalyst (red) and 20% Pt/C (blue) for the ORR measured in O_2 saturated seawater (solid) and 0.1 M KOH (dash) at 400 rpm and (b) cyclic voltammetric analysis of ORR measurement in N_2 (dash) and O_2 saturated (solid) condition for seawater between 0.4 to -0.4 V at 5 mV s^{-1} .

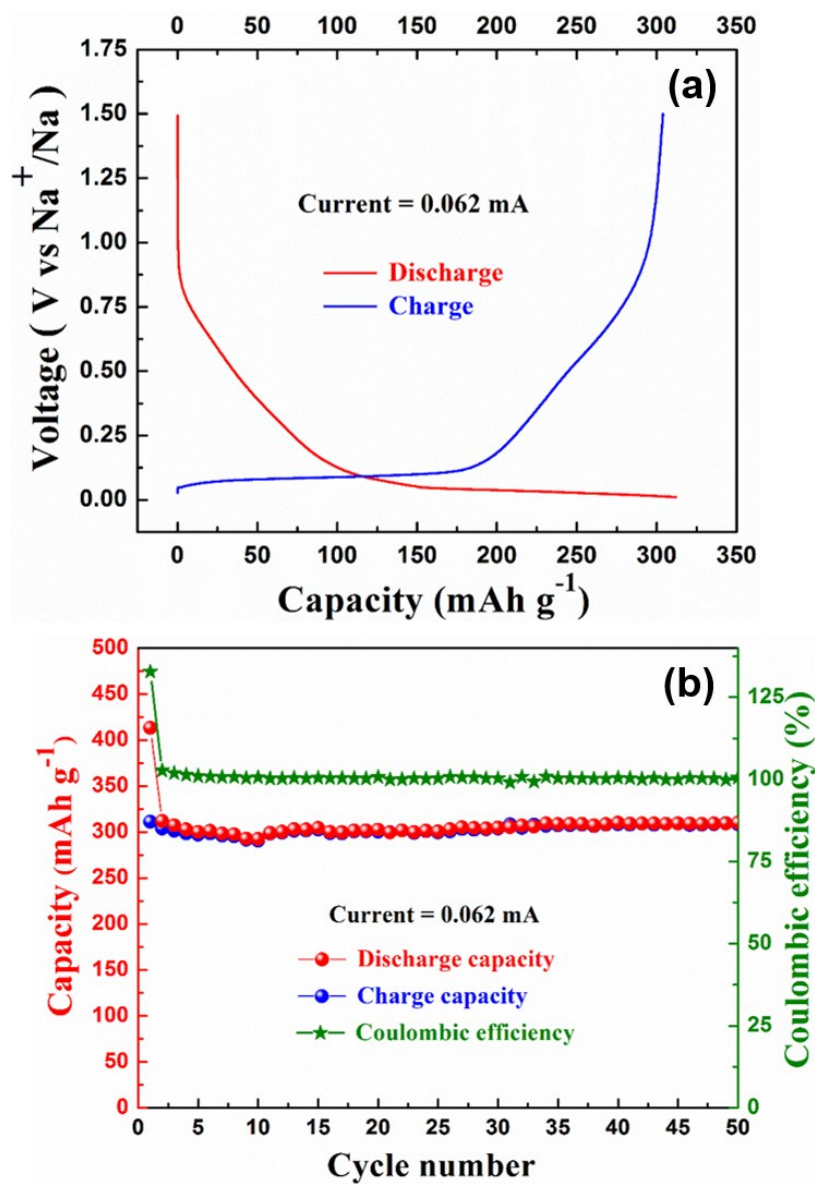


Fig. S5 Na-ion half-cell performance of the hard carbon (HC) anode: (a) voltage vs capacity and (b) capacity vs cycle number performance of fabricated coin type Na-ion half-cell (Na vs HC) cycled in between 0.01 to 1.5 V at 0.062 mA for 50 cycles using non-aqueous 1 M NaPF₆ in 1:1 (v/v) EC-PC with FEC (5% wt.) additive electrolyte.