

Supporting Information for

Cu₃(PO₄)₂: Novel Anion Convertor for Aqueous Dual-Ion Battery

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S1 Experimental Section

Cu₃(PO₄)₂ was synthesized by a facile precipitation reaction. Stoichiometric amounts of CuCl₂·2H₂O and Na₃PO₄ were firstly dissolved in distilled water, respectively. Na₃PO₄ solution was then dropped into CuCl₂ solution under continuous stirring and the suspension was formed. After aged for 24 h, the sky blue precipitates were filtered and washed with distilled water until the presence of chloride ions could not be detected in the filtrate.

Na_{0.44}MnO₂ was prepared by a simple solid state method. Stoichiometric amounts of Na₂CO₃ (5 mol% excess) and Mn(CH₃COO)₂·4H₂O were ball milled at 500 rpm for 12 h and subsequently heated in air at 900 °C for 10 h to yield the product.

The morphology of Cu₃(PO₄)₂ was recorded by scanning electron microscopy (SEM; Hitachi SU-70). The X-ray diffraction (XRD) pattern of Cu₃(PO₄)₂ was collected using an X-ray diffractometer (Bruker D8 Advance) equipped with a Cu K α radiation source. TG analysis was conducted using a NETZSCH STA409 PG/PC instrument.

Three-electrode cells were used to assess the electrochemical performance of Cu₃(PO₄)₂. For the fabrication of the working electrodes, Cu₃(PO₄)₂ was blended with acetylene black and polytetrafluoroethylene in the weight ratio of 8:1:1. Subsequently, the mixture was pressed into sheets and pasted onto carbon papers for testing. The counter and reference electrodes were platinum foil and Ag/AgCl (3 M KCl), respectively. The electrolyte was 0.75 M Na₂HPO₄ aqueous solution. All the

electrochemical characterizations of $\text{Cu}_3(\text{PO}_4)_2$ were conducted on a LANHE CT2001A battery test system.

S2 Supplementary Figures

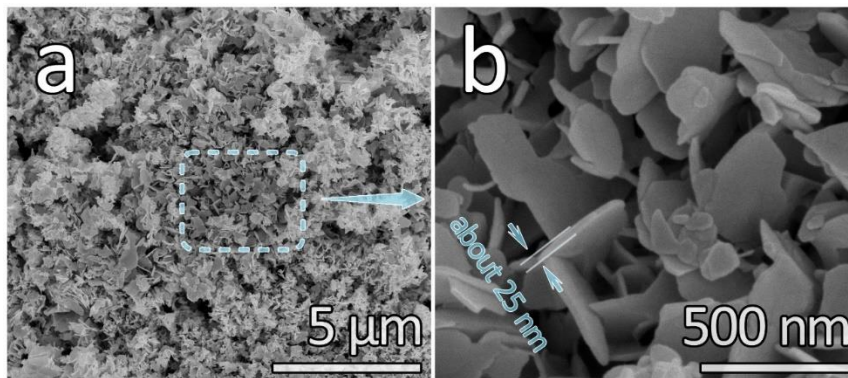


Fig. S1 SEM images of $\text{Cu}_3(\text{PO}_4)_2$

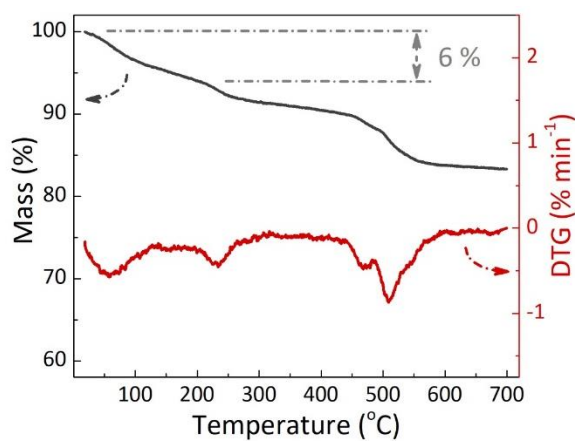


Fig. S2 TG curve of $\text{Cu}_3(\text{PO}_4)_2$ powder

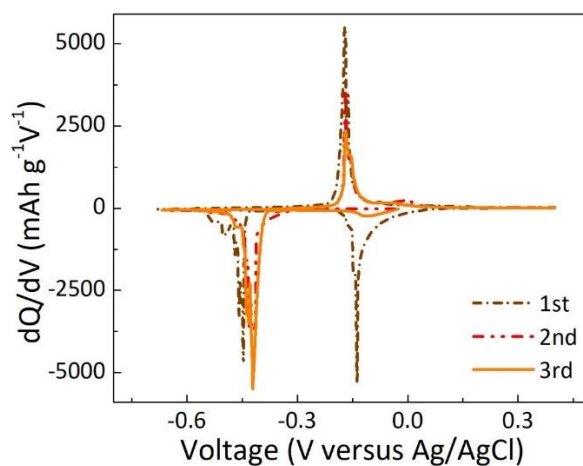


Fig. S3 Differential dQ/dV plots of $\text{Cu}_3(\text{PO}_4)_2$ between -0.7 and 0.4 V versus Ag/AgCl in the initial three cycles

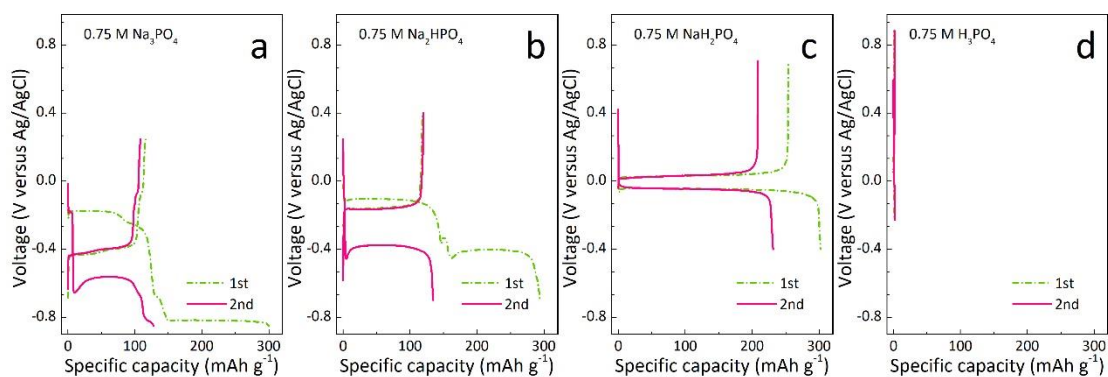


Fig. S4 Galvanostatic discharge/charge profiles of $\text{Cu}_3(\text{PO}_4)_2$ electrode at 50 mA g^{-1} in electrolytes with different concentration of OH^- ions: **a** $0.75 \text{ M Na}_3\text{PO}_4$; **b** $0.75 \text{ M Na}_2\text{HPO}_4$; **c** $0.75 \text{ M NaH}_2\text{PO}_4$; **d** $0.75 \text{ M H}_3\text{PO}_4$

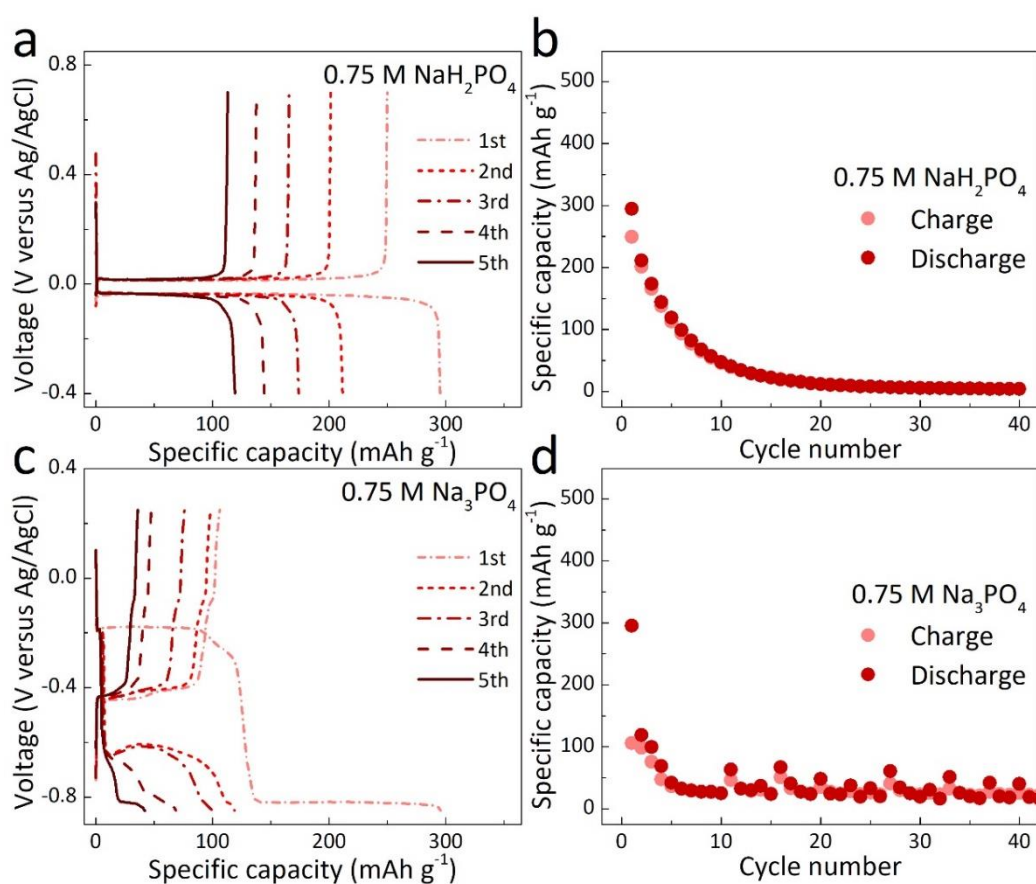


Fig. S5 Galvanostatic discharge/charge profiles and the corresponding cycling performances of $\text{Cu}_3(\text{PO}_4)_2$ electrode at 50 mA g^{-1} in electrolytes with different concentration of OH^- ions: **a, b** $0.75 \text{ M NaH}_2\text{PO}_4$; **c, d** $0.75 \text{ M Na}_3\text{PO}_4$

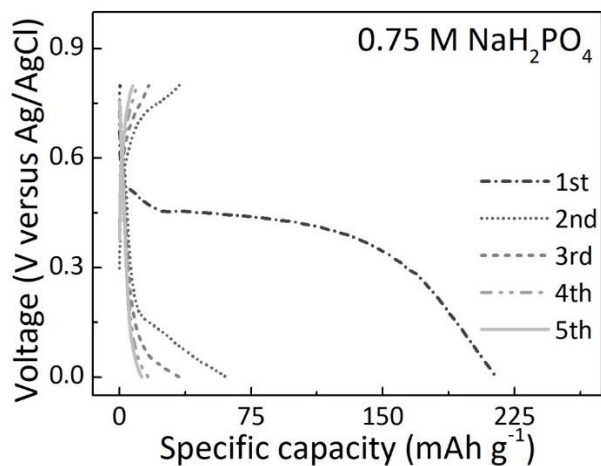


Fig. S6 Galvanostatic discharge/charge profiles of $\text{Na}_{0.44}\text{MnO}_2$ in 0.75 M NaH_2PO_4 aqueous solution

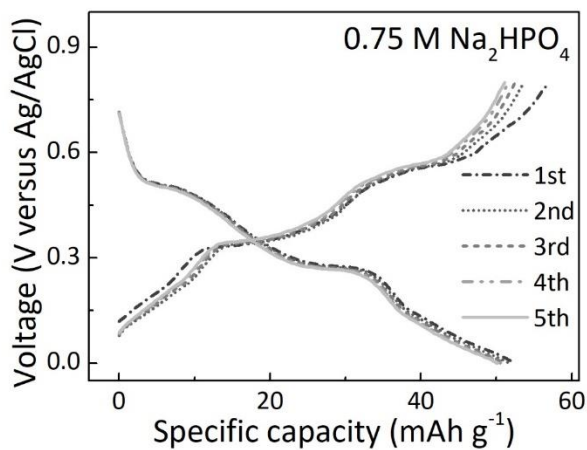


Fig. S7 Galvanostatic discharge/charge profiles of $\text{Na}_{0.44}\text{MnO}_2$ in 0.75 M Na_2HPO_4 aqueous solution

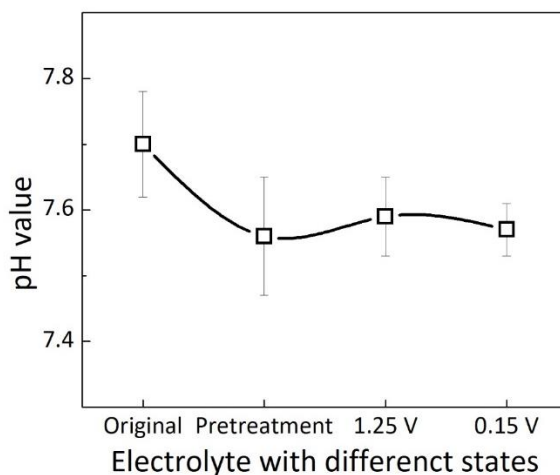


Fig. S8 Variation for pH value of electrolyte during cycling in pretreated $\text{Cu}_3(\text{PO}_4)_2/\text{Na}_{0.44}\text{MnO}_2$ dual-ion cell

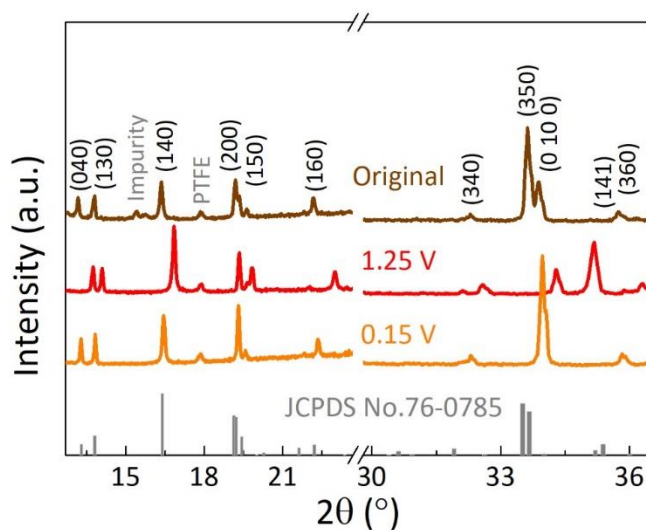


Fig. S9 XRD patterns of $\text{Na}_{0.44}\text{MnO}_2$ electrode in pretreated $\text{Cu}_3(\text{PO}_4)_2/\text{Na}_{0.44}\text{MnO}_2$ dual-ion cell during cycling

According to previous references [36, 44], $\text{Na}_{0.44}\text{MnO}_2$ is isostructural with $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$. Therefore, we use $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$ to match with $\text{Na}_{0.44}\text{MnO}_2$.

Table S1 Comparison for operating voltage of pretreated $\text{Cu}_3(\text{PO}_4)_2/\text{Na}_{0.44}\text{MnO}_2$ dual-ion cell in this work with other cells in the literatures

Cell	Operating voltage (V)	References
$\text{Na}_{0.44}\text{MnO}_2//\text{pretreated Cu}_3(\text{PO}_4)_2$	0.70 & 0.45	This work
K20// TiS_2 -10CNT	~0.4	[38]
$\text{MnO}_2//\text{Ag}$	~0.4	[40]
S//Fe	~0.36	[41]
$\text{Na}_{0.44}\text{MnO}_2//\text{BiOCl}$	0.35	[39]
$\text{Na}_2\text{Mn}_5\text{O}_{10}/\text{AgCl}$	0.3	[23]
$\text{FePO}_4//\text{Ag}$	~0.2	[40]
$\text{FePO}_4//\text{Ag}$	~0.2	[42]
S//Cu	~0.15	[43]