Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A high-voltage aqueous lithium ion capacitor with high energy density from alkaline-neutral electrolyte

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Calculation details:

The discharge specific capacitances (C_s) of single electrodes or supercapacitors were calculated from the GCD curves using the following **Equation (S1)**:[1]

$$C_s = \frac{I \times t}{m \times \Delta V}\ (F\ \mathrm{g}^{-1}) \tag{S1}$$

where I is the discharge current (A), t is the discharge time (s), C_s is the specific capacitance (F g^{-1}), ΔV is the discharge potential window including IR drop (V) and m is the mass or total mass of active electrode material (g).

The mass ratios of the positive and negative electrodes were balanced according to the following **Equation (S2)**:[2]

$$\frac{m_+}{m_-} = \frac{C_- \Delta V_-}{C_+ \Delta V_+} \tag{S2}$$

During the galvanostatic charge/discharge of supercapacitors, the energy density (*E*) and power density (*P*) were calculated by the following **Equations (S3)** and **(S4)**:[3]

$$E = \frac{C_s \times \Delta V^2}{2 \times 3.6}\ (\mathrm{W\ h\ kg}^{-1}) \tag{S3}$$

$$P = \frac{E \times 3600}{t}\ (\mathrm{W\ kg}^{-1}) \tag{S4}$$

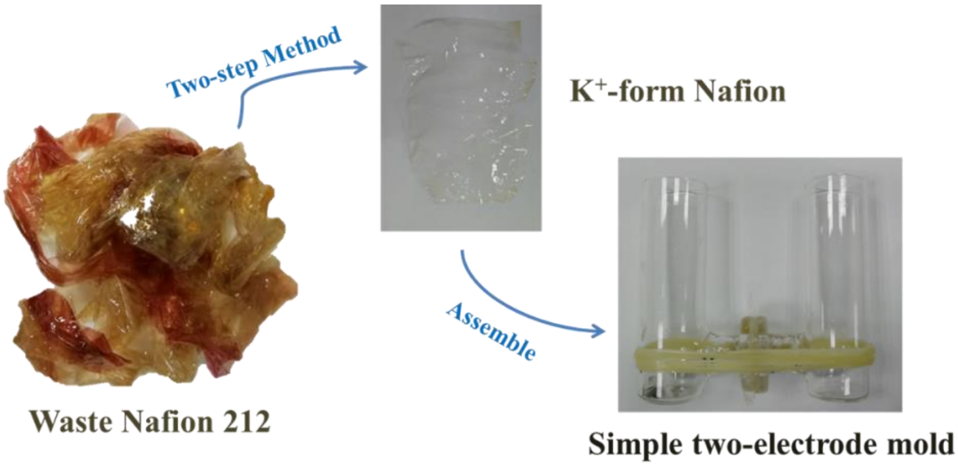

Fig. S1: Construction of a simple two-electrode mold.

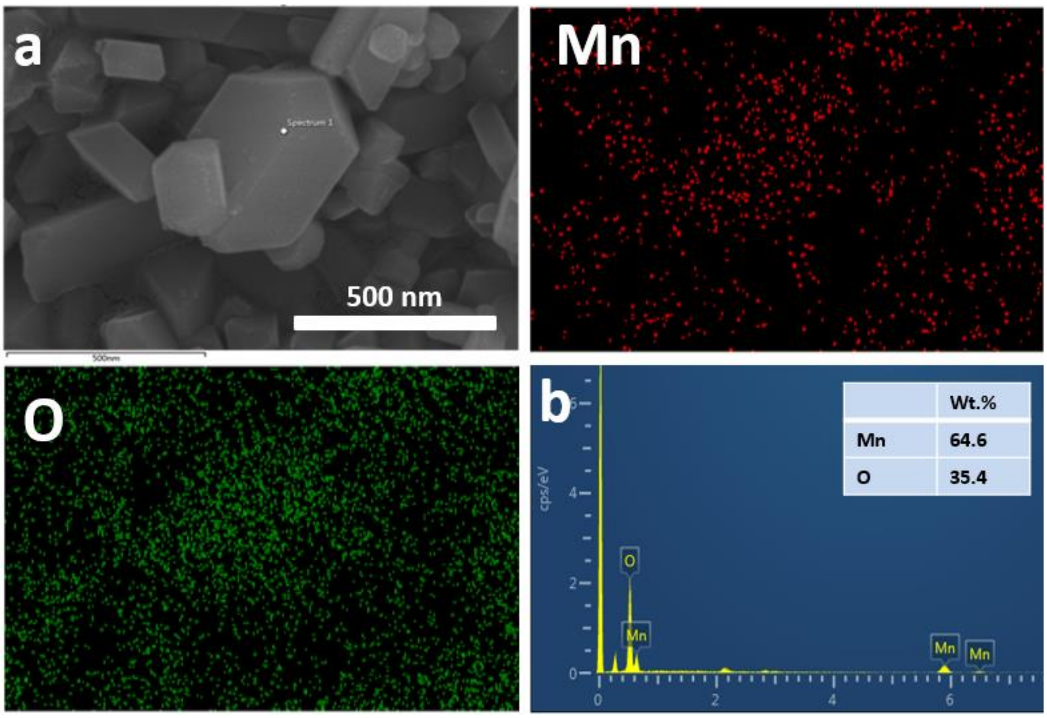

Fig. S2: The EDS elemental mapping (a) and spectrum (b) of $LiMn_2O_4$ nanorods (tested by HITACHI S4800).

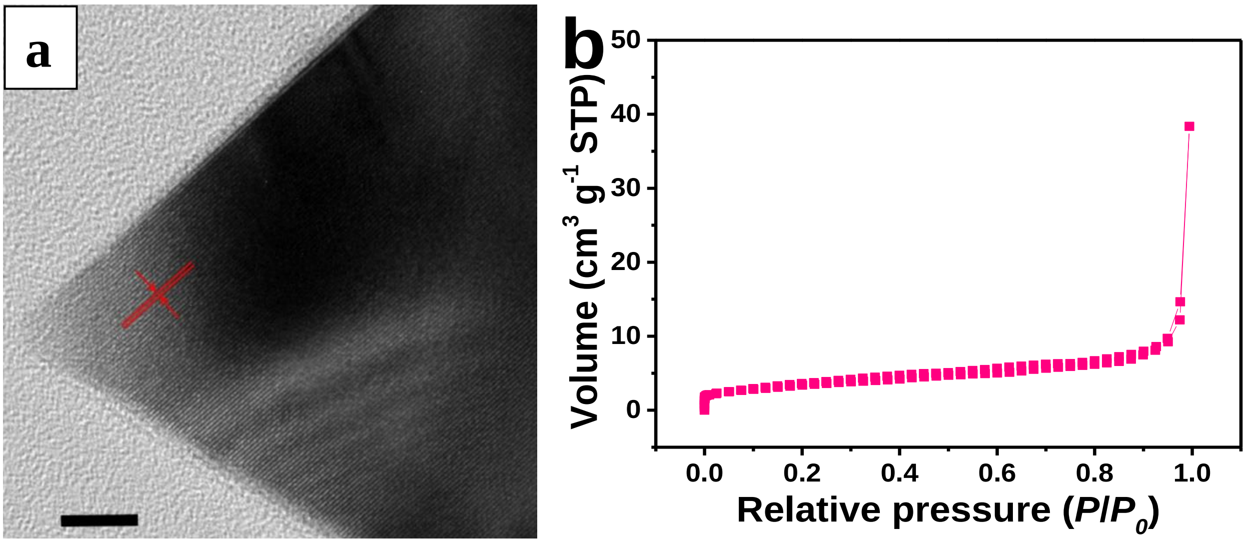

Fig. S3: (a) High-magnification TEM image of $LiMn_2O_4$ nanorods (The lattice spacing is ~0.48 nm). Scale bars: 10nm (b) N_2 absorption-desorption isotherm.

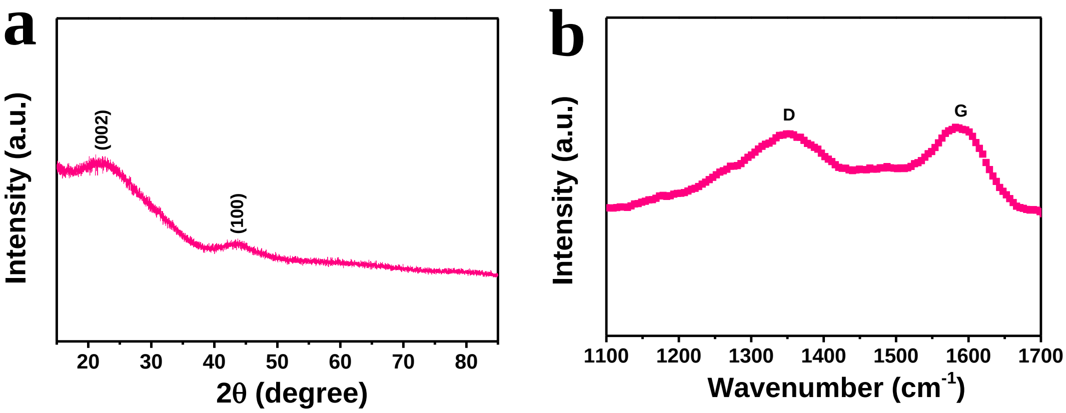

Fig. S4: (a) XRD patterns and (b) Raman spectra of NBC.

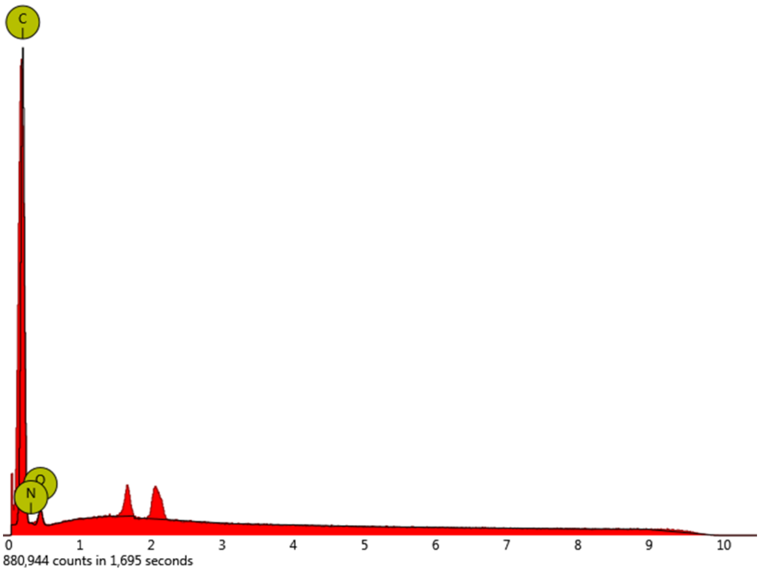

Fig. S5: The EDS elemental spectrum of NBC (tested by Phenom ProX).

Table S1: The element contents of NBC from EDS elemental spectrum.

NBC	C	N	O
wt.%	83.00	6.45	10.55
At.%	86.06	**5.73**	8.21

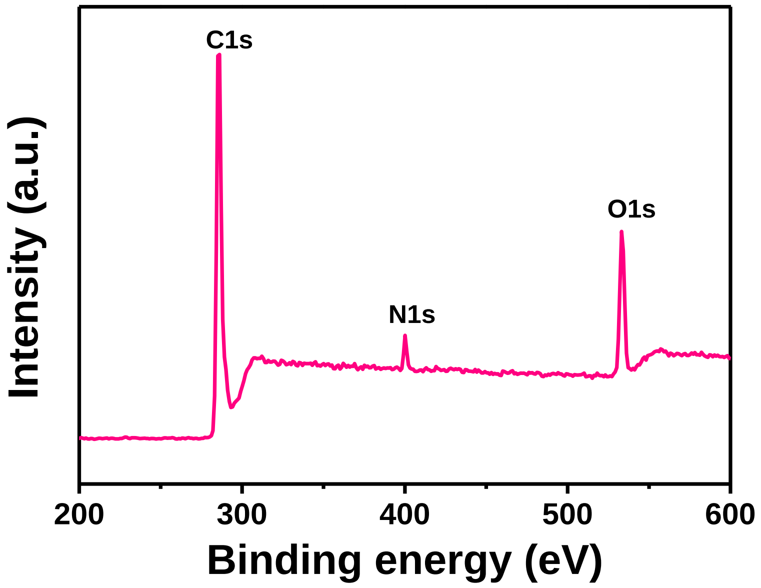

Fig. S6: XPS spectra of NBC.

The atomic contents of C, N, and O in NBC from the XPS spectra are about 86.48%, 4.42% and 9.10%, respectively, which is close to the values from EDS elemental spectrum.

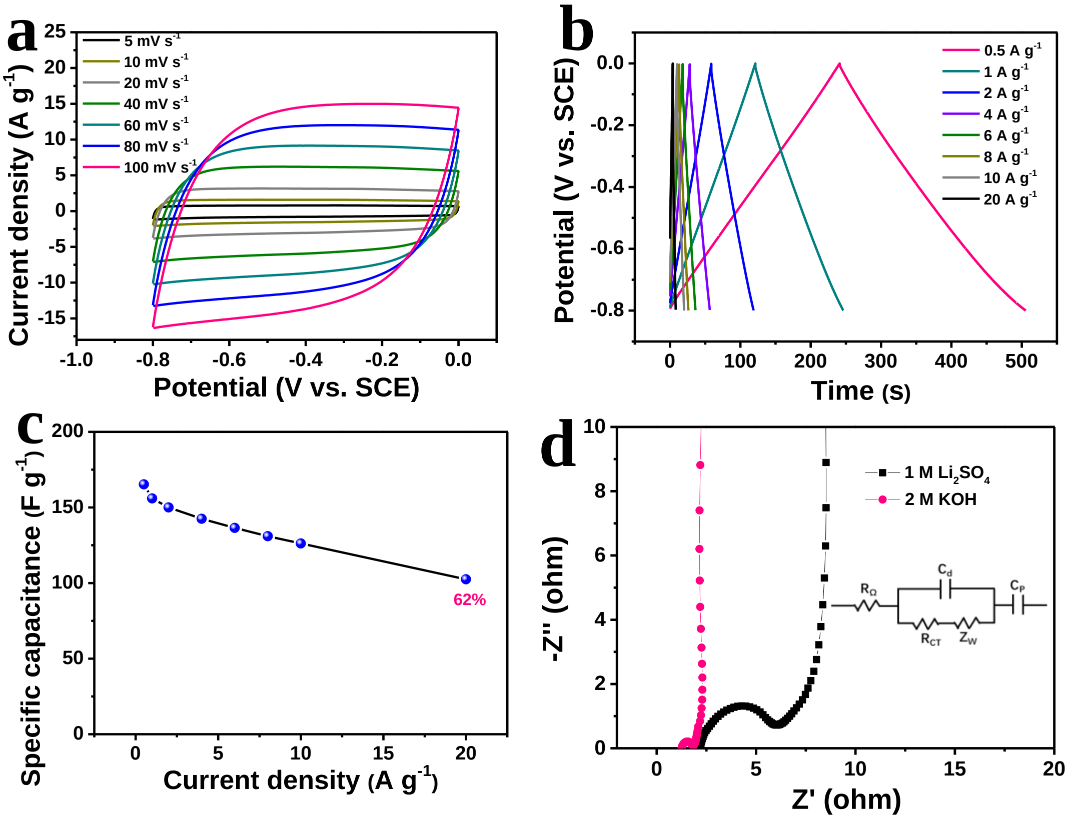

Fig. S7: (a) CV curves of NBC electrode at various scan rates in 1 M Li_2SO_4 aqueous electrolyte solution. (b) GCD profiles of NBC electrode at different current densities. (c) Specific capacitance vs. current densities. (d) Nyquist plots of NBC electrodes in 1 M Li_2SO_4 and 2 M KOH aqueous electrolyte solutions (inset is equivalent circuit model). (The mass of active material is 0.87 mg)

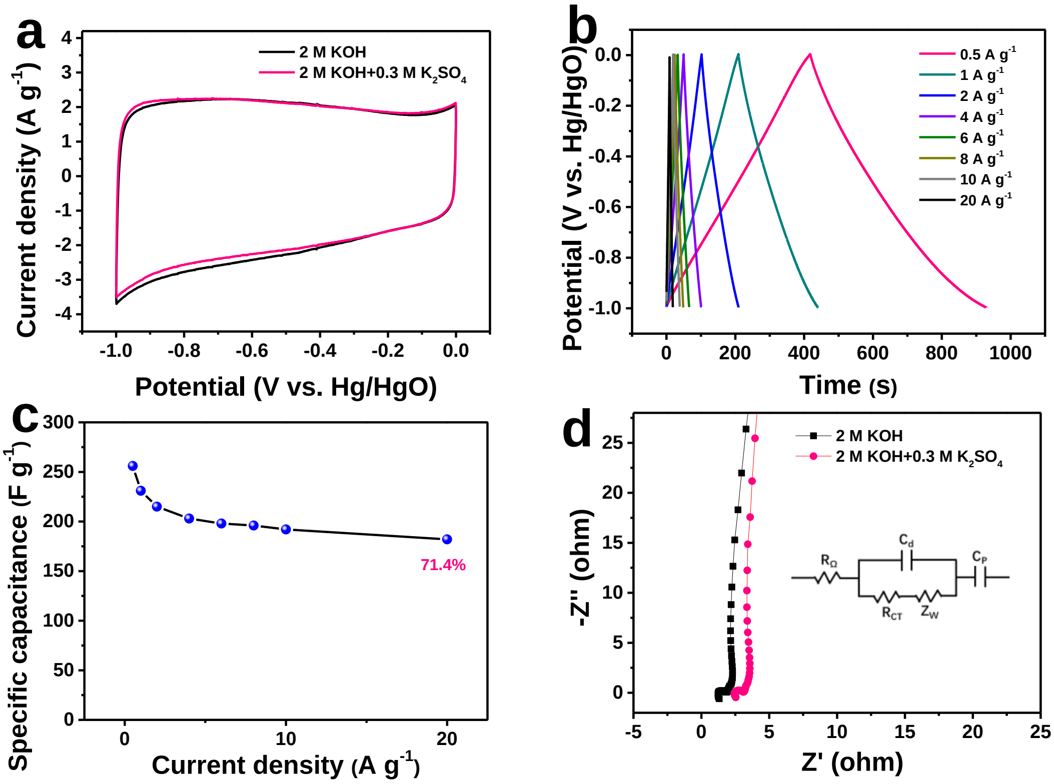

Fig. S8: Electrochemical performance of NBC electrode in 2 M KOH (0.3 M K_2SO_4) aqueous electrolyte: (1) CV comparison at 10 mV s^{-1} in 2 M KOH and 2 M KOH (0.3 M K_2SO_4). (b) GCD profiles at different current densities. (c) Specific capacitance vs. current densities. (d) Nyquist plots in 2 M KOH and 2 M KOH (0.3 M K_2SO_4) (inset is equivalent circuit model). (The mass of active material is 1.09 mg)

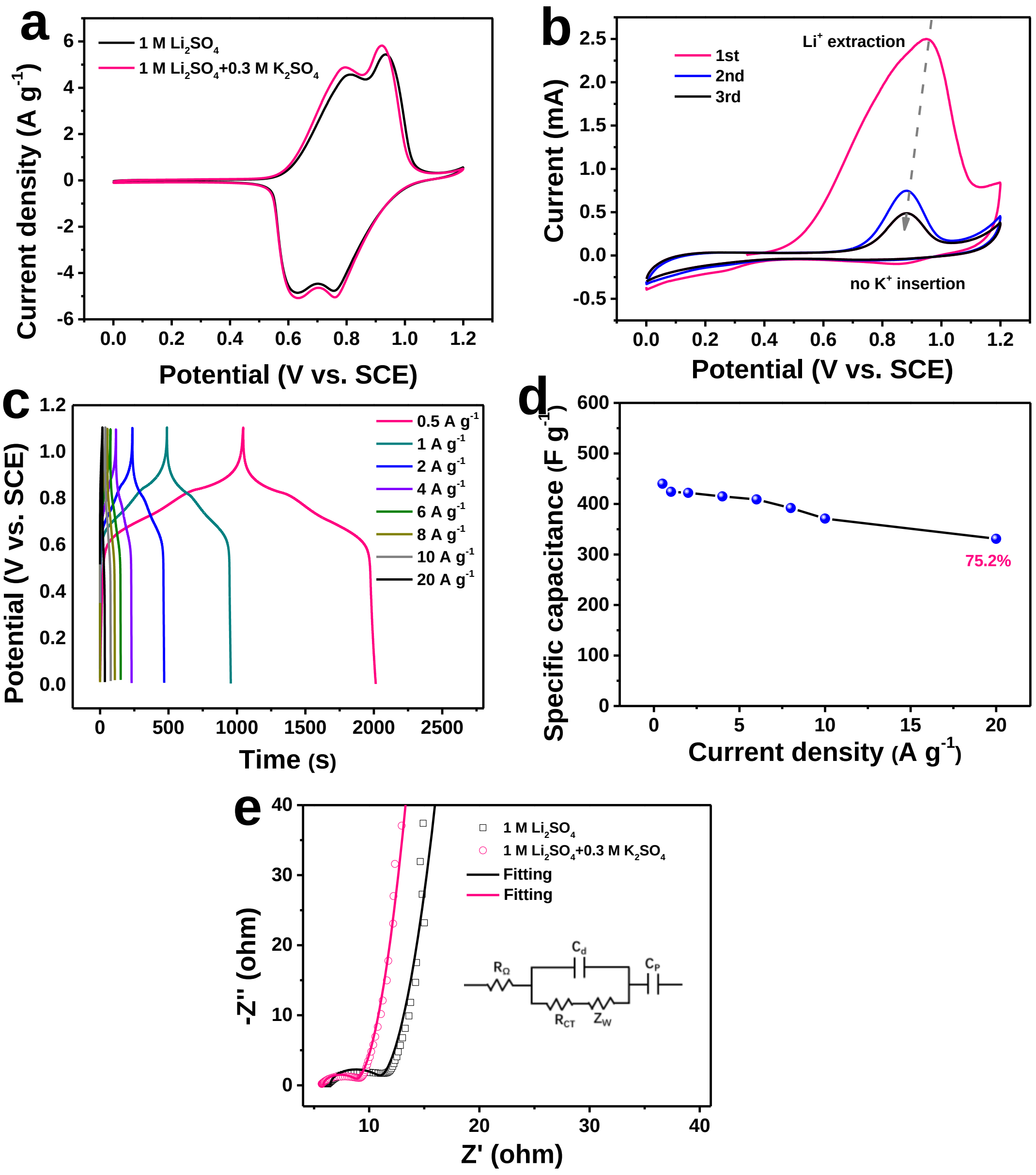

Fig. S9: Electrochemical performance of LiMn$_2$O$_4$ electrode in 1 M Li$_2$SO$_4$ (0.3 M K$_2$SO$_4$) aqueous electrolyte: (a) CV comparison at 3 mV s^{-1} in 1 M Li$_2$SO$_4$ and 1 M Li$_2$SO$_4$ (0.3 M K$_2$SO$_4$). (b) The first three CV curves of LiMn$_2$O$_4$ electrode at 3 mV s^{-1} in 0.3 M K$_2$SO$_4$. (c) GCD profiles at different current densities. (c) Specific capacitance vs. current densities. (d) Fitting Nyquist plots in 1 M Li$_2$SO$_4$ and 1 M Li$_2$SO$_4$ (0.3 M K$_2$SO$_4$) (inset is equivalent circuit model). (The mass of active materials in 0.3 M K$_2$SO$_4$ and the mixed electrolyte are 0.8 and 1.2 mg, respectively)

In Fig. S9b, a obvious oxidation peak can be found and it gradually gets smaller with CV cycles, which should be ascribed to the Li$^+$ extraction from LiMn$_2$O$_4$ nanorods. Moreover, there are no reduction peaks in CV curves, further indicating that no K$^+$ insertion exists in. The addition of K$_2$SO$_4$ only brought a little K$^+$ absorption capacitance.

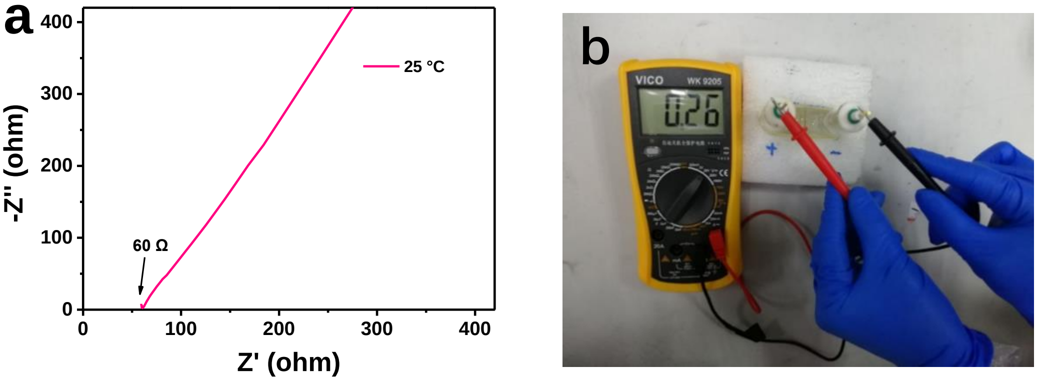

Fig. S10: (a) EIS result of Pt//Pt with 0.3 M K_2SO_4 aqueous electrolyte. (b) The potential difference of two electrolytes (Pt//Pt) in the alkaline-neutral system (about 0.26 V).

In Fig. S8a, a bulk resistance (the intercept of the straight line on the real axis) of 60 Ω can be obtained. According the following Equation (S5):[4]

$$\sigma = \frac{l}{A \times R_B}\ (S\ cm^{-1}) \tag{S5}$$

where, σ is the ionic conductivity, l is the thickness of the film (0.135 mm), A is the area of the electrolyte contacting with the film (0.25 cm^2), R_b is the bulk resistance, the caculated K^+ ionic conductivity is 9×10^{-4} S cm^{-1}, which can be approximated as the K^+ ion conductivity of the K^+ ion conductive membrane.

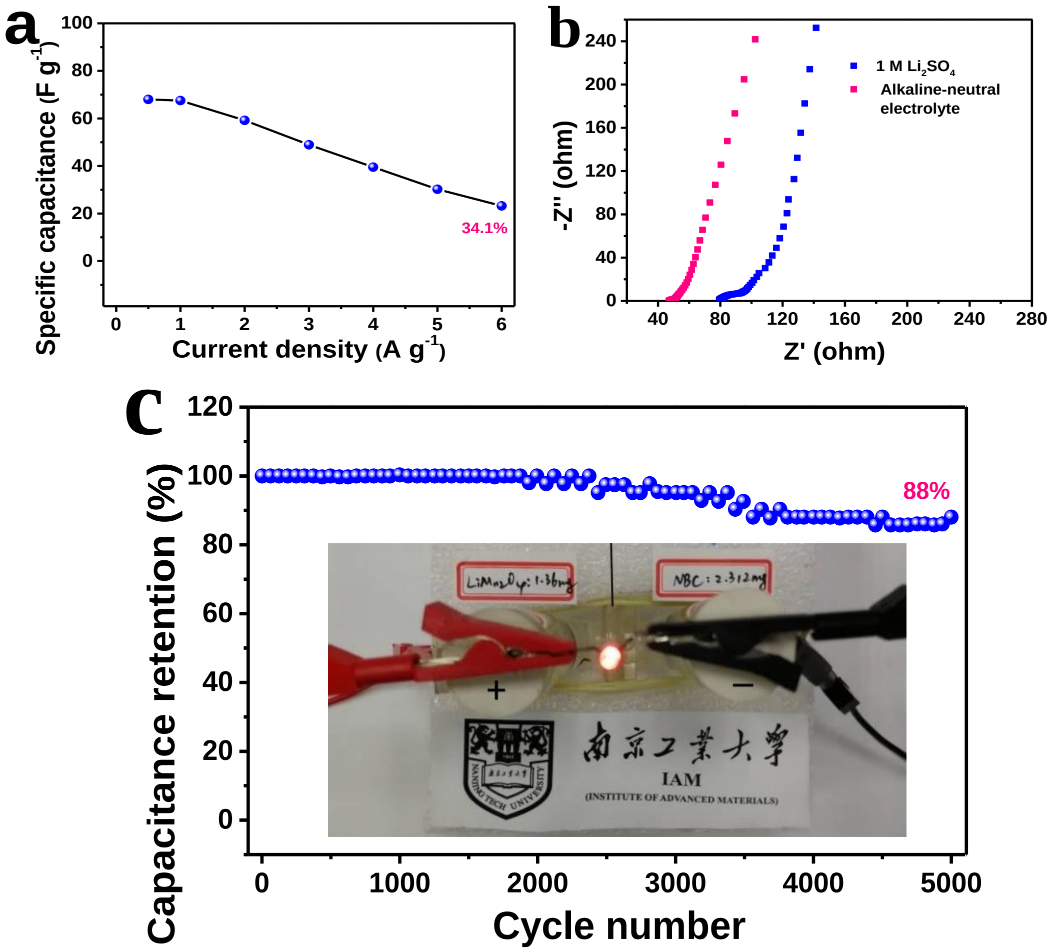

Fig. S11: (a) Discharge specific capacitance of the NBC//$LiMn_2O_4$ LIC with the alkaline-neutral electrolyte at various current densities. (b) Nyquist plots of NBC//LiMn2O4 LICs with two various electrolytes. (c) Cycling stability of the LIC (inset is optical image of one cell lighting up a red LED).

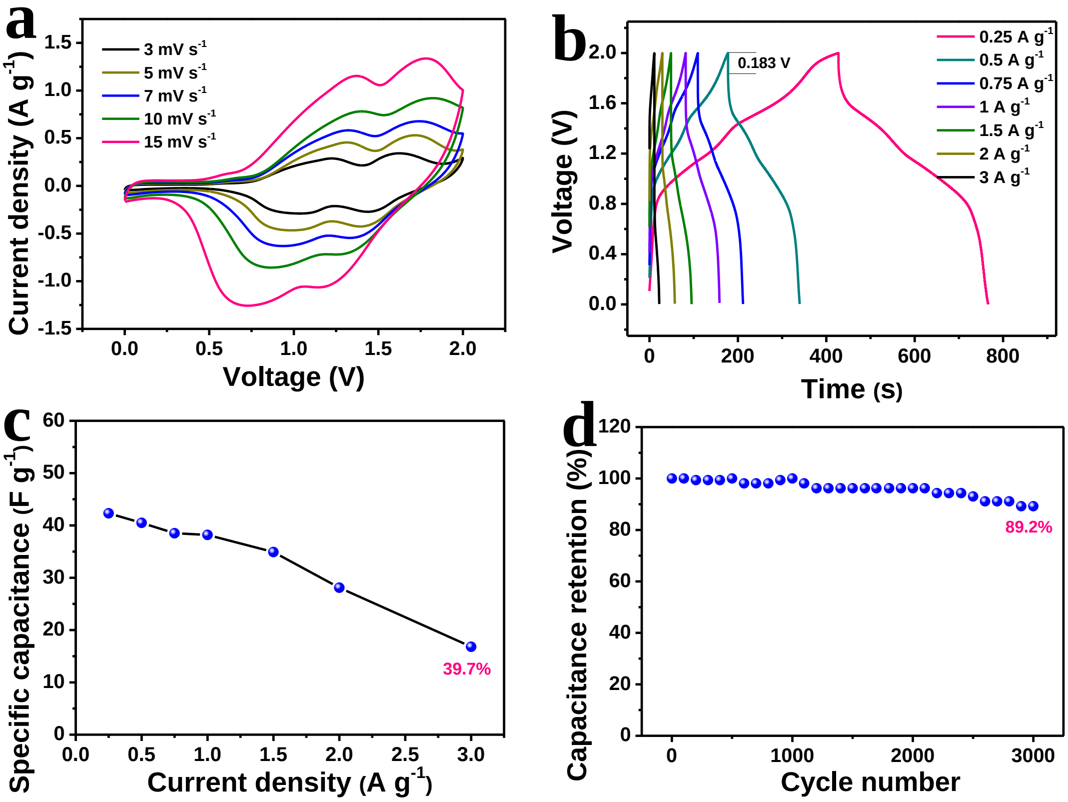

Fig. S12: a) CV curves of the NBC//$LiMn_2O_4$ LIC with Li_2SO_4 aqueous electrolyte solution at various scan rates. b) GCD profiles of the NBC//$LiMn_2O_4$ LIC at different current densities. c) Specific capacitance vs. current densities. d) Cycling performance of the NBC//$LiMn_2O_4$ LIC at a current density of 1 A g^{-1}. (The total mass of active materials is 3.03 mg)

References:

[1] T. Zhai, L. M. Wan, S. Sun, Q. Chen, J. Sun, Q. Y. Xia, H. Xia, *Adv. Mater.*, 2017, **29**, 1604167.
[2] Z. J. Fan, J. Yan, T. Wei, L. J. Zhi, G. Q. Ning, T. Y. Li, F. Wei, *Adv. Funct. Mater.*, 2011, **21**, 2366-2375.
[3] W. H. Zuo, C. Y. Xie, P. Xu, Y. Y. Li, J. P. Liu, *Adv. Mater.*, 2017, **29**, 1703463.
[4] J. Malathi, M. Kumaravadivel, G. Brahmanandhan, M. Hema, R. Baskaran, S. Selvase -karapandian, *J. Non. Cryst. Solids*, 2010, **356**, 2277-2281.