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## A Sodium-Aluminum Hybrid Battery

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**Fig. S1.** Cyclic voltammograms of electrolytes  $EMIC-AlCl_3$  (1-1.3) (a and c) and 1.0 M  $NaAlCl_4/EMIC-AlCl_3$  (1-1.3) (c and d) on a Pt (a and b) and  $Na_3V_2(PO_4)_3$  (c and d) at a scan rate of 20 mV/s (a and b) and 0.1mV/s (c and d), respectively.



Fig. S2 Charge/discharge profile (a and c) and cycling stability (b and d) of the hybrid battery  $Al||Na_3V_2(PO_4)_3$  in EMIC-AlCl<sub>3</sub> (1-1.1) (a and b) and EMIC-AlCl<sub>3</sub> (1-1.3) (c and d) at a current rate of C/5. (The active material loading for a and b is 1.7 mg/cm<sup>2</sup>, whereas the active material loading for c and d is 1.8 mg/cm<sup>2</sup>).



Fig. S3 Charge/discharge profile (a) and cycling stability (b) of the hybrid battery  $Al||Na_3V_2(PO_4)_3$ in 1.0 M NaAlCl<sub>4</sub>/EMIC-AlCl<sub>3</sub> (1-1.3) at a current rate of C/5. (The active material loading is 1.1 mg/cm<sup>2</sup>).



Fig.S4 XRD sample for Na extraction in carbonate electrolyte.



Fig. S5 XRD sample for (a) Na extraction in carbonate electrolyte and (b) Na insertion in ionic liquid electrolyte. The coulombic efficiency between Na insertion and Na extraction is 93.5%.



Fig. S6 Comparison of the charge/discharge profile of the hybrid battery Al $||Na_3V_2(PO_4)_3$  in 2.0 M NaAlCl<sub>4</sub>/EMIC-AlCl<sub>3</sub> (1-1.3) at a current rate of 1C at 25 °C and 50°C. (The active material loading is 1.1 mg/cm<sup>2</sup>).