Electronic Supplementary Information

Metal-ion batteries meet supercapacitors: high capacity and high rate capability rechargeable batteries with organic cathodes and Na/K alloy anode

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Experimental section

Synthesis of P1: 5,10-dihydrophenazine (6 mmol, 1.09 g), palladium acetate (0.12 mmol, 27 mg), 1,4-dibromobenzene (6 mmol, 1.415 g), sodium tert-butoxide (15 mmol, 1.44 g) in 60 mL of *o*-xylene were mixed in a Schlenk flask. The mixture was purged with Ar for 15 minutes. Tri-tert-butylphosphine (0.24 mmol, 58 μL) in 5 mL of *o*-xylene was then added. The mixture was then thoroughly purged with Ar for 10 minutes refluxed for 12 hours. The mixture was cooled to r.t., the solid was separated by filtration and washed with MeOH, H_2O, chlorobenzene, diethyl carbonate using Soxhlet extraction. The solid was vacuum-dried at 70 °C for 12 hours. Elemental composition: found (% wt.): C – 80.25, N – 8.81, H – 4.825, Br – 0.00; calculated for $C_{18}H_{12}N_2$ (% wt.): C – 84.38, N – 10.94, H – 4.688, Br – 0.00. ^{13}C MAS ssNMR (101 MHz): 139.6, 135.6, 130.0, 121.2, 113.1 ppm. FTIR (KBr): 558, 620, 733, 817, 919, 1010, 1060, 1158, 1267, 1335, 1484, 1600 cm^{-1}.

Synthesis of P2: 3,3’-diaminobenzidine tetrahydrochloride (3 mmol, 1080 mg) and hexaketocyclohexane octahydrate (2 mmol, 624 mg) were placed in a round-bottom flask with 50 mL of N-methylpyrrolidone. Concentrated H_2SO_4 (20 μL) was added to the mixture. The system was evacuated/refilled with Ar (3 times) and then refluxed for 8 hours. After the mixture was cooled to r.t., the solid was filtered and thoroughly washed with N,N-dimethylacetamide and acetone via Soxhlet extraction. The solid was vacuum-dried at 150 °C overnight. Elemental composition: found (% wt.): C – 64.25, N – 17.81, H – 3.97; calculated for tetrahydrate $C_{24}N_6H_9(H_2O)_4$ (% wt.): C – 63.57, N – 18.53, H – 3.78. ^{13}C MAS ssNMR (101 MHz): 141.8, 129.2 ppm. FTIR (KBr): 589, 622, 663, 724, 795, 825, 890, 1086, 1148, 1192, 1357, 1490, 1615, 1659, 2927, 3061, 3227, 3390 cm^{-1}.

Materials characterization: FTIR spectra were recorded with a PerkinElmer Spectrum BX spectrometer using KBr pellets. Elemental analysis was performed via express gravimetry with Elementar vario MICRO cube. The MASS ssNMR spectroscopy measurements were carried out on a Bruker AVANCE III spectrometer, which operates at 101 MHz for ^{13}C nuclei. The chemical shifts were referenced to tetramethylsilane at 0 ppm by adjusting the signal of adamantane spinning at 8 kHz to 38.48 ppm. Conventional cross-polarization was utilized for ^{13}C NMR spectra acquisition, the spinning rate was 15 kHz. Energy-dispersive X-ray spectroscopy (EDX) was carried out using Zeiss LEO SUPRA 25 miscroscope with integrated EDX detector.

Electrode preparation: to prepare the cathode electrodes, active materials, carbon black (Super P) and poly(vinylidene difluoride) (PVdF) with the mass ratio of 4:4:2 were mixed with N-methylpyrrolidone to form homogeneous slurries, which were then tape-casted onto aluminium foil, dried and calendered at r.t. The composite mass loading was ~1.8–2.5 mg cm^{-2}

(active material mass loading 0.7–1 mg cm^{-2}). The electrodes were cut into disks (diameter 10 mm), which were then used for cell assembling.

NaK-based anode preparation: Sodium was from Sigma Aldrich (ACS reagent, dry). Potassium was from Sigma Aldrich (chunks in mineral oil, 98% trace metals basis), and it was washed with heptane and dried in Ar-filled glovebox. For both metals, outer oxide layers of the chunks were removed with a knife, so the surfaces of the metal pieces were shiny. Weight ratio of K:Na was 85:15. Sodium was added on top of potassium, and the liquid alloy formed spontaneously at r.t. The resulting droplet was covered with an oxide layer (Fig. S1). To purify the alloy, a portion of it was taken with an automatic pipette from the inside of the droplet, so no substance from the surface of the droplet was picked. The resulting shiny liquid (Fig. S1) was used for the anode preparation.
Sigracet 28 AA carbon paper (thickness 190±30 µm, areal weight 55±10 g m^{-2}, porosity ~85% basing on the density of graphite $\rho = 2.266$ g cm^{-3}) was cut into circles (Fig. S2), which were when heated to 150–200 ˚C inside an Ar-filled glovebox. NaK alloy was added on top of the circles (40 µL NaK per ~18-20 mg carbon paper), and after about a minute the alloy reacted with carbon, forming an orange potassium intercalation compound, and impregnated into the electrode (Fig. S2).

Cell assembling and testing: CR2032-type coin cells were assembled in an Ar-filled glovebox with O_2 level <1 ppm. Saturated solution of KPF_6 (~1.5м) in dry 1,2-dimethoxyethane was used as the electrolyte (70 µL of electrolyte per cell added), glass fiber (Whatman GF/A Glass microfiber filters, GE Healthcare) was used as the separator. Galvanostatic cycling was carried out with Neware battery testing systems. Voltage windows were 2.5–4.5 V for **P1** and 1.1–3.6 V for **P2**. Measurements were carried out at room temperature.

Calculations: Coulombic efficiency was calculated as the ratio between charge and discharge capacities multiplied by 100%. Specific capacities, energy and power densities shown in the main text were calculated basing on the mass of the active materials **P1** or **P2**. The contribution to the capacity from Super P was negligible in the selected voltage ranges.
Specific energy E_s was defined as:

$$E_s = \int_0^{Q_m} E(q)dq$$

where Q_m is the discharge specific capacity per material mass unit (**P1**, **P2** etc.), $E(q)$ is the dependence of the potential vs. NaK on the specific capacity during discharge (i.e. the discharge curve shown in Fig. 2 of the main text), dq is specific capacity changing upon discharge.
Power density was calculated as the energy density divided by time required for discharge.
To calculate the specific capacities including the mass of counter-ions participating in redox processes (PF_6^- for **P1**, K^+ for **P2** etc.), i.e. calculate the capacity per mass unit of discharged (for rocking-chair type batteries) or charged (for dual-ion batteries) states, the following formula was used:

$$Q_{with\ counter\ ions} = \frac{Q_m}{(1 + \frac{Q_m}{F} M_{ci})}$$

where Q_m is the specific capacity per material mass unit (**P1**, **P2** etc.), F is the Faraday constant, M_{ci} is the molar mass of the counter-ion. Specific energy and power (Chart S1) were recalculated accordingly, using $Q_{\text{with counter ions}}$ instead Q_m.

P2 electrode preparation for EDX analysis: **P2**-based electrodes were discharged, charged and discharged again at 200˚mA˚g^{-1} current density. The cells were disassembled in Ar-filled glovebox, thoroughly washed with pure dimethoxyethane and dried at room temperature.

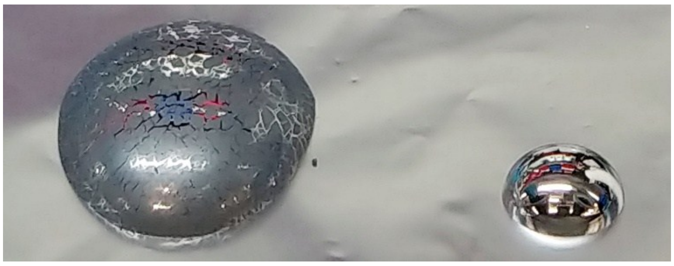

Fig. S1. NaK alloy droplets formed after mixing Na and K (left) and after purification (right).

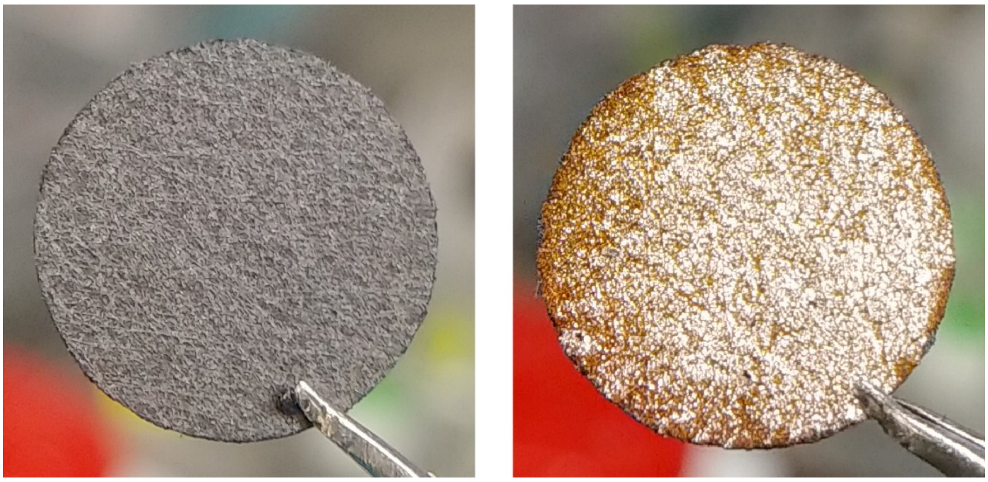

Fig. S2. Carbon paper disk (left) and NaK-based electrode after its reaction with the liquid alloy (right).

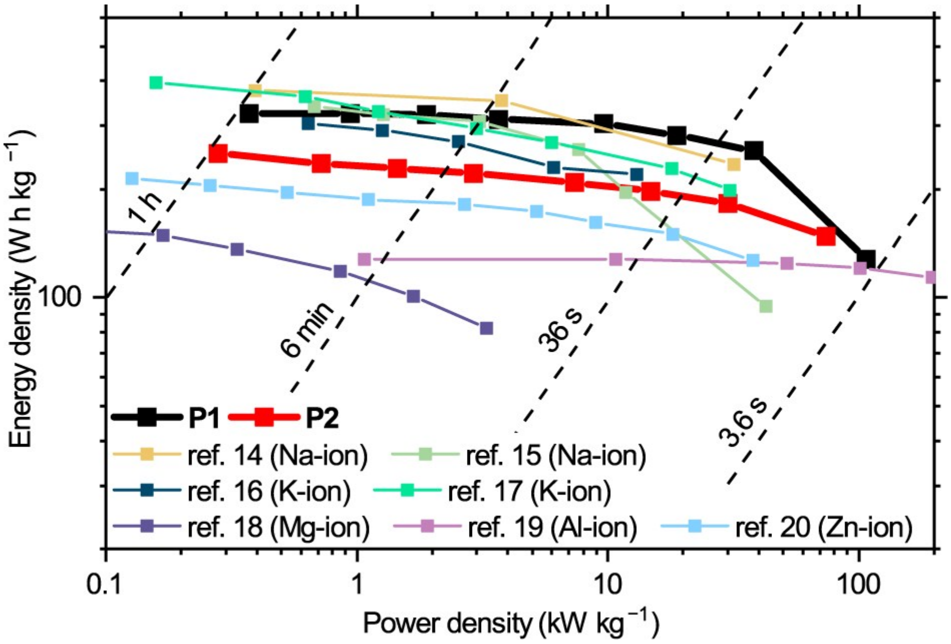

Chart S1. Ragone plots featuring the characteristics of polymeric cathodes **P1** and **P2** versus other types of state-of-the-art cathode materials for high-power lithium-free batteries reported in the literature. Calculation includes the mass of counter-ions participating in the charge-discharge process (i.e., mass of PF_6^- included for **P1**, mass of K^+ included for **P2** etc.).

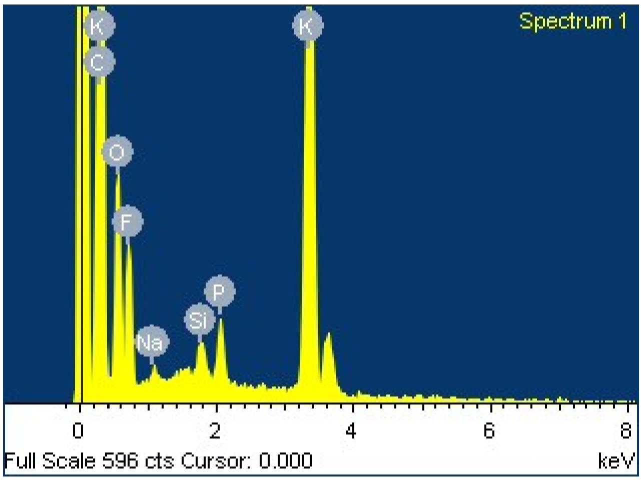

Chart S2. EDX spectrum of **P2**-based electrode in the discharged state.

Table S1. Elemental composition of **P2**-based electrode in the discharged state.

Element	Weight%	Weight% Sigma	Atomic%
C	43.51	0.87	59.95
O	17.45	0.66	18.05
F	11.37	0.55	9.90
Na	0.28	0.10	0.20
Si	0.76	0.11	0.45
P	1.63	0.14	0.87
K	25.01	0.52	10.58
Total	100.00		