

An Organic Anode for High Temperature Potassium-Ion Batteries

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The wide applications of rechargeable batteries require state-of-the-art batteries that are sustainable (abundant resource), tolerant to high-temperature operations, and excellent in delivering high capacity and long-term cycling life. Due to the scarcity and uneven distribution of lithium, it is urgent to develop alternative rechargeable batteries. Herein, an organic compound, azobenzene-4,4'-dicarboxylic acid potassium salts (ADAPTS) is developed, with an azo group as the redox center for high performance potassium-ion batteries (KIBs). The extended π -conjugated structure in ADAPTS and surface reactions between ADAPTS and K-ions enable the stable charge/discharge of K-ion batteries even at high temperatures up to 60 °C. When operated at 50 °C, ADAPTS anode delivers a reversible capacity of 109 mAh g⁻¹ at 1C for 400 cycles. A reversible capacity of 77 mAh g⁻¹ is retained at 2C for 1000 cycles. At 60 °C, the ADAPTS-based KIBs deliver a high capacity of 113 mAh g⁻¹ with 81% capacity retention at 2C after 80 cycles. The exceptional electrochemical performance demonstrates that ADAPTS is a promising electrode material for high-temperature KIBs.

The advancement of energy storage technology has stimulated the wide applications of rechargeable batteries in portable electronics, electric vehicles, and smart grids.^[1–3] Due to the applications in the deserts and tropical countries, a wide working temperature range, especially high temperature, is pivotal for the rechargeable batteries.^[4,5] Unfortunately, achieving an

exceptional battery performance is still a significant challenge at high temperatures due to the structural degradation caused by the fast transfer of alkali-ions.^[4] Therefore, Li-ion batteries have been intensively investigated as high temperature batteries owing to the smallest ion size of Li among the alkali-ions.^[4,5] Nevertheless, the scarcity and unevenly global distribution of Li resource is an obstacle for the further development of Li-ion batteries.^[3,6]

One promising strategy to replace Li-ion batteries is developing high-temperature K-ion batteries (KIBs), which have distinguished advantages among alkali-ion batteries, e.g., the significantly more abundance of K than Li (2.09 vs 0.0017 wt% in the Earth crust) and lower redox potential of K⁺/K than Na⁺/Na (−2.93 vs −2.71 V).^[3,6,7] All these merits ensure KIBs provide clean energy with low cost and high energy density.


However, the larger ion size of K⁺ than Li⁺ and Na⁺ results in a significant structural deterioration for the conversion and intercalation electrodes. The conversion electrodes suffer from a large volume change that is tremendously significant in KIBs,^[4,8,9] while the capacity of the intercalation electrodes is very low.^[10,11] As reported by Amine's group, stabilizing the material surface is the key factor for cycling Li-ion batteries at high temperatures such as 55 °C.^[12] Thus, it is extremely challenging for KIB electrodes to withstand a temperature above 55 °C, due to the less stable solid electrolyte interphase (SEI) compared to the Li counterpart.^[13]

Herein, we designed an organic anode that stores K-ions through surface reaction for high-temperature KIBs beyond the current operating temperature of 55 °C with high rate capability and long cycle life. Azobenzene-4,4'-dicarboxylic acid potassium salts (ADAPTS) with a redox center of azo group (N=N) is selected to reversibly react with K⁺, as shown in **Figure 1a**. Different from the conversion and intercalation reactions, ADAPTS with surface reaction can largely retain the structural stability during the reversible electrochemical reactions between azo group and K⁺ even at a high temperature. Furthermore, organic compounds are ideal electrode materials for clean energy applications since they are inexpensive and sustainable.^[14,15] At the ambient temperature, the ADAPTS anode delivers a reversible capacity of 109 mAh g⁻¹ at 0.1C for 100 cycles and a long-term cycle life of 1000 cycles is achieved

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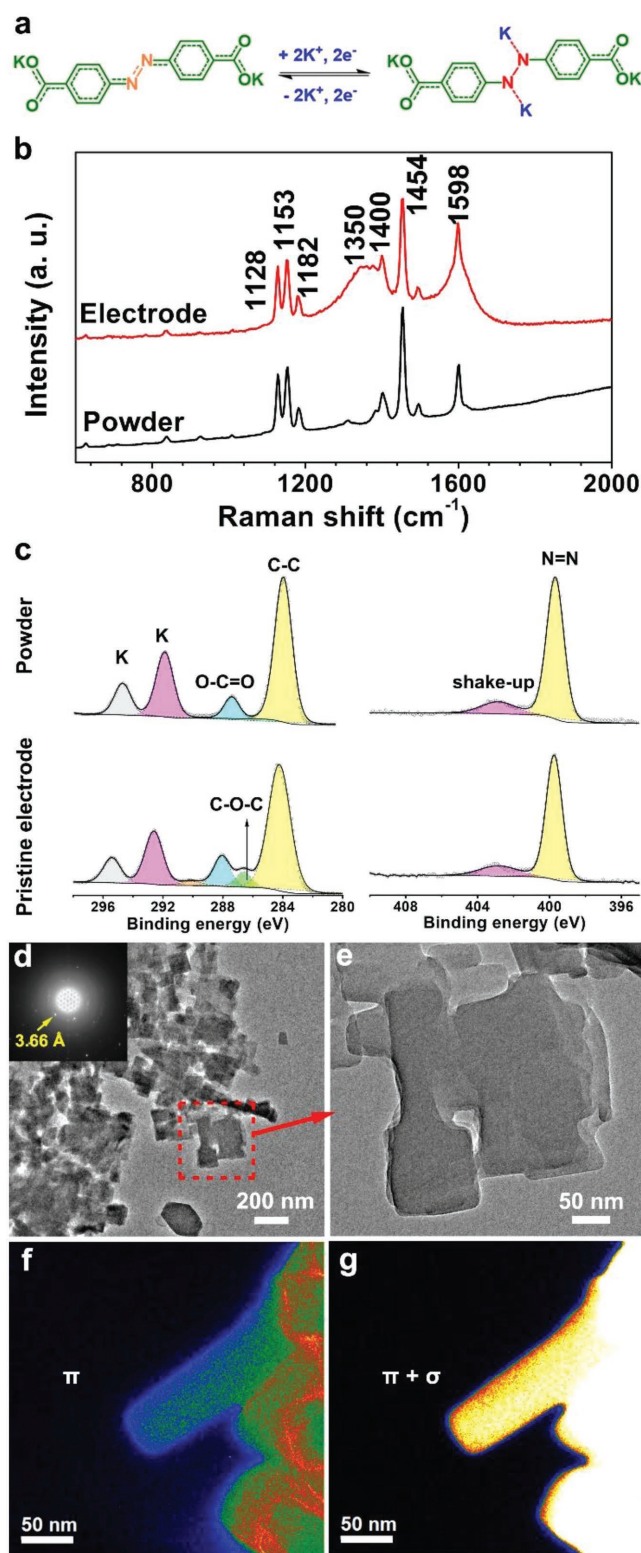


Figure 1. a) Reaction paths of ADAPTS during charge/discharge in KIBs; b) Raman spectrum of the ADAPTS powders; c) XPS C 1s and N 1s spectra of ADAPTS powder and electrode; TEM images of ADAPTS compound with SAED pattern as the inset d) and the HRTEM image e); EELS spectra of ADAPTS compound at low f) and high g) energy loss regimes.

at a high current densities of 1C and 2C. When operated at high temperatures, the reaction kinetics can be accelerated with minimal structural deterioration, which is distinct from the reported conversion and intercalation electrodes. At 50 °C, the ADAPTS anode exhibits a reversible capacity of 109 mAh g^{-1} for 400 cycles at 1C with a very slow capacity decay rate of 0.059% per cycle. When further increasing the temperature to 60 °C, the ADAPTS-based KIBs deliver a high capacity of 113 mAh g^{-1} with 81% capacity retention at 2C after 80 cycles. To the best of our knowledge, this work is the first report of KIBs operated at 60 °C.

The ADAPTS were synthesized by neutralizing the azobenzene-4,4'-dicarboxylic acid with potassium hydroxide. The introduction of carboxylate groups can significantly reduce the dissolution of ADAPTS into the organic electrolytes, which is a key factor for the exceptional electrochemical performance in the electrochemical tests.^[16] This neutralization method by converting the carboxylic acids into carboxylates is an effective strategy to enhance the polarity of the organic active materials,^[17] and thus, minimize the dissolution of organic compounds into the electrolytes. The nuclear magnetic resonance (NMR) cartelization validates the molecular structure of ADAPTS (Figure S1, Supporting Information). In ^1H NMR, the chemical shift at 4.784 is from solvent (D_2O). The two doublet peaks around 8 ppm are stemmed from the two groups of H in the benzene rings. The ^{13}C NMR also confirms C atoms in five different chemical environments. The C atoms connected to azo groups correspond to the peak at 153.728 ppm, while the peak at 139.331 ppm represents the C atoms link to carboxylate groups. The rest of the C atoms in the benzene rings lead to the peaks at 130.037 and 122.403 ppm. The C atoms in carboxylate group display the peak at 174.833 ppm.

The ADAPTS molecular structure is further elucidated by mass spectrum, Raman spectrum and X-ray photoelectron spectroscopy (XPS). The main peak at $m/z = 268.92$ in mass spectrum (Figure S2, Supporting Information) refers to the formula of $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4^{2-}$. The two peaks at 1128 and 1182 cm^{-1} in Raman spectrum (Figure 1b) are ascribed to the stretching of phenyl-N.^[18] The peak at 1153 cm^{-1} represents the symmetrical bend of azo group.^[19] Peaks at 1400 and 1454 cm^{-1} further validate the N=N group.^[18,19] The structure of ADAPTS is also supported by the XPS measurements (Figure 1c). The peaks are calibrated by the C-C peak at 284.8 eV in C 1s spectrum. Two peaks in C 1s spectra (292 and 295 eV) are attributed to the K 2p signals in ADAPTS powder and pristine electrode.^[20] The N=N and shake up features at 400 and 403 eV can be observed in N 1s spectra in powder and pristine electrodes.^[21] The N=N group in ADAPTS is the redox center for electrochemical reaction with K-ion, providing a theoretical capacity of 155 mAh g^{-1} . All the NMR, mass spectra, Raman spectrum, and XPS confirm the molecular structure of ADAPTS in Figure 1a. In addition to the ADAPTS compound, two distinct peaks at 1350 and 1598 cm^{-1} in the Raman spectrum of ADAPTS electrode are attributed to the disordered carbon (D band) and graphitic carbon (G band) in carbon black, respectively.^[8,19] The G band overlaps with the phenyl ring peak.^[19]

The ADAPTS powders exhibit lamellar morphology, as depicted in scanning electron microscopy (SEM, Figure S3, Supporting Information) and transmission electron microscopy

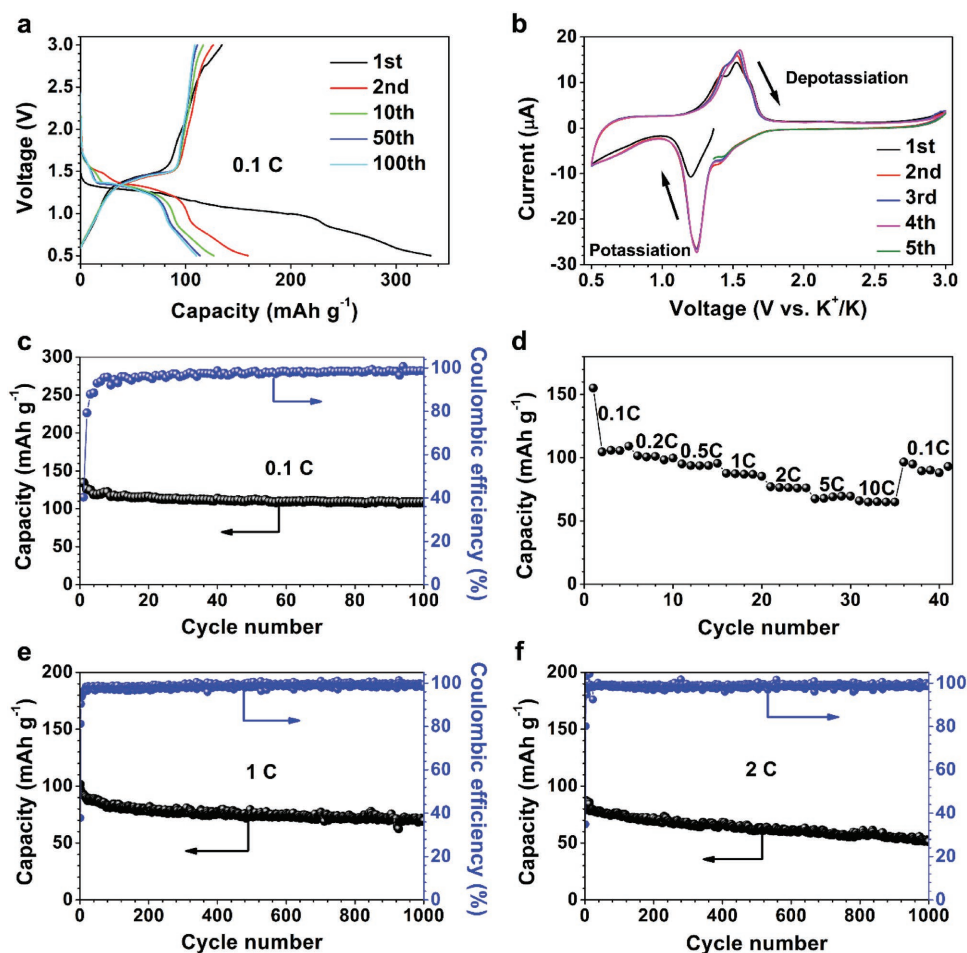


Figure 2. The electrochemical performance of ADAPTS anode in K-ion batteries at room temperature. a) Galvanostatic charge/discharge profiles obtained at 0.1C; b) cyclic voltammograms at 0.1 mV s⁻¹; c) Depotassiation capacities with corresponding Coulombic efficiencies achieved at 0.1C; d) Rate performance at different C rates; Charge capacities and Coulombic efficiencies measured at 1C e) and 2C f).

(TEM, Figure 1d,e) images. The elemental mappings of ADAPTS demonstrate that the K, N, C, and O are uniformly distributed in the compound (Figure S4, Supporting Information). The ADAPTS powder has high crystallinity as demonstrated by the selected area electron diffraction (SAED) pattern in the inset of Figure 1d. This is consistent with the XRD pattern (Figure S5, Supporting Information). ADAPTS has a large conjugated structure, which can provide a strong driving force, π - π interaction, to form crystals.^[15,22] The lamellar structure is further supported by the high resolution TEM (HRTEM) image (Figure 1e) of the highlighted area in Figure 1d. The delocalized electrons can be observed by electron energy loss spectroscopy (EELS) (Figure 1f,g and Movie S1, Supporting Information). At low energy loss regime, signals from π electrons are pronounced (Figure 1f). At high energy loss region, both π and σ electrons can be observed (Figure 1g). EELS line scan profiles are provided to further support the mappings, as shown in Figure S6, in the Supporting Information. Site B in Figure S6a in the Supporting Information is measured by EELS with Site A as the reference. Consistent with Figure 1f,g, the peak representing π electrons is observed at the low region and a distinct peak at the high energy loss region is attributed to

π and σ electrons (Figure S6b, Supporting Information). The delocalized π electrons can enhance the electron transfer in ADAPTS, which further improves the fast charge/discharge capability.^[16,23,24] Therefore, ADAPTS is a promising anode material for high-temperature KIBs.

The electrochemical performance of ADAPTS electrode was measured by galvanostatic charge/discharge at 0.1C (1C = 155 mA g⁻¹) between 0.5 and 3.0 V (Figure 2a). The initial Coulombic efficiency (ICE) is 40.3% due to the formation of SEI, but it is quickly enhanced in the following cycles after the formation of a stable SEI layer. Two discharge plateaus at 1.43 and 1.24 V correspond to the two cathodic peaks in cyclic voltammetry (CV, Figure 2b). One charge plateau at 1.5 V in Figure 2a is consistent with two adjacent anodic peaks at 1.46 and 1.55 V in Figure 2b. This suggests a two-step reaction between two potassium ions and one azo group.

As shown in Figure 2c–f, the ADAPTS anode displays a long cycle life and high capacity at room temperature. At 0.1C, ADAPTS delivers an initial reversible capacity of 134 mAh g⁻¹, and the reversible capacity remains at 109 mAh g⁻¹ after 100 cycles (Figure 2c). The anode can retain a capacity of 66 mAh g⁻¹ at 10C, demonstrating the high-rate performance

(Figure 2d). The long-term cycling tests were performed at high current densities of 1C and 2C. At 1C, the ADAPTS anode exhibits a reversible capacity of 70 mAh g⁻¹ after 1000 cycles with a very slow capacity decay rate of 0.038% per cycle (Figure 2e). At 2C, it delivers a reversible capacity of 51 mAh g⁻¹ after 1000 cycles with a very slow capacity decay rate of 0.049% per cycle (Figure 2f). The fast charge and discharge capability and long cycle life are attributed to the extended π -conjugated structure of ADAPTS.^[1,23] In Movie S2 in the Supporting Information, a demonstration is provided to show that the coin cell with ADAPTS anode can charge a stopwatch in practical applications.

The performances of ADAPTS anode at high temperatures of 50 and 60 °C were evaluated. The solvents in the electrolyte are a combination of ethylene carbonate (EC) and diethyl carbonate (DEC), because both solvents have relatively high boiling points compared to the other typical solvents used in the electrolytes.^[25] EC has been reported to facilitate the formation of robust SEI on the anode, which can improve the cycling stability at high temperatures. DEC was used due to the high temperature limit of 120 °C and a low melting point to compensate EC.^[25] The charge/discharge curves (Figure 3a,b) at

50 and 60 °C are similar to that at the ambient temperature, while the reversible capacities at high temperatures are higher than those at the ambient temperature due to the faster reaction kinetics. At 50 °C, the initial charge capacity of ADAPTS is 138 mAh g⁻¹ at 1C, and a reversible capacity of 109 mAh g⁻¹ is retained after 400 cycles, corresponding to a slow capacity decay rate of 0.059% per cycle (Figure 3c). At 2C, a reversible capacity of 77 mAh g⁻¹ is retained after 1000 cycles, demonstrating the excellent cycling stability of the ADAPTS anode at high temperature (Figure 3d). The CE of ADAPTS at 50 °C is close to 100% during the long-term cycling test. The ADAPTS anode also shows superior performance at 60 °C. A reversible capacity of 113 mAh g⁻¹ can be retained at 2C after 80 cycles (Figure 3e), corresponding to a capacity retention of 81% of the initial capacity. At a high current density of 4C, a reversible capacity of 98 mAh g⁻¹ is retained after 90 cycles (Figure 3f), and the CE is close to 100%. A control test was conducted with the graphite anode for high-temperature (50 °C) KIBs at the current density of 1C. As shown in Figure S7 in the Supporting Information, the high temperature cycle life of the graphite anode is much worse than that of ADAPTS anode. Therefore, the exceptional electrochemical performance at ambient and

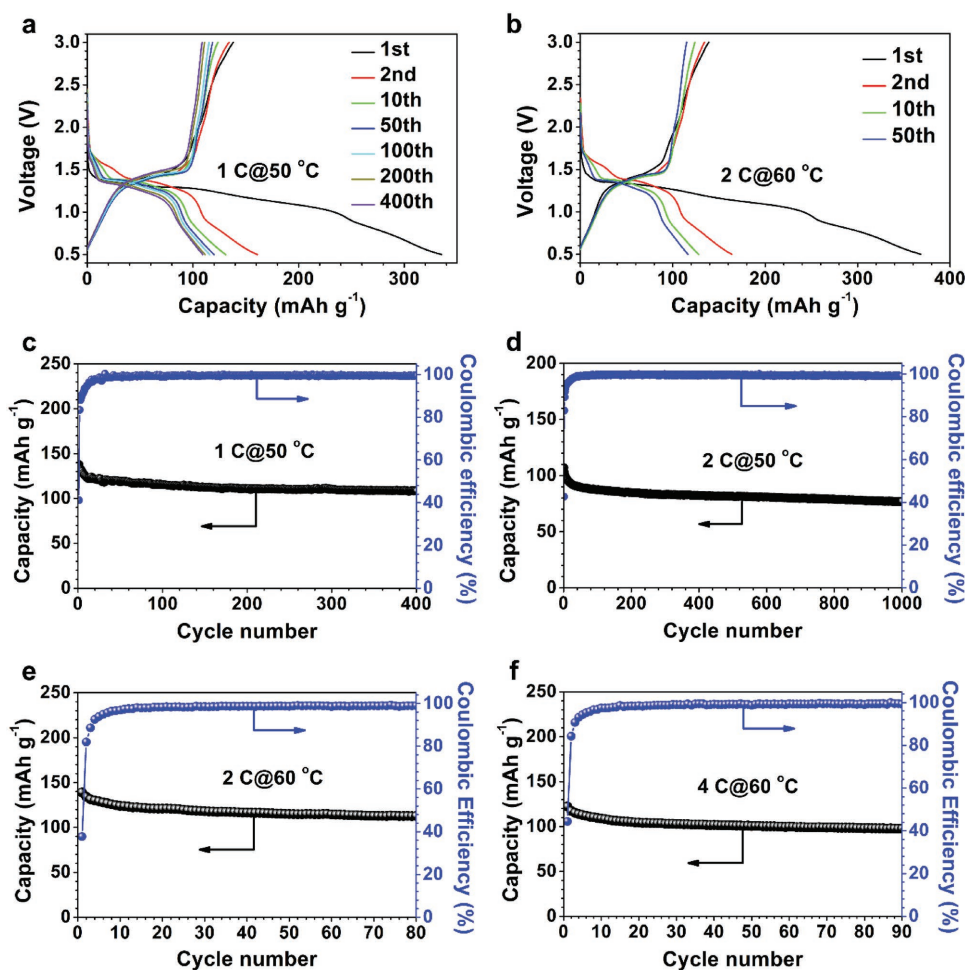


Figure 3. The electrochemical performance of ADAPTS anode in K-ion batteries at high temperatures. Galvanostatic charge/discharge profiles obtained at 1C under 50 °C a) and 2C under 60 °C b); Depotassiation capacities with corresponding Coulombic efficiencies achieved under 50 °C at 1C c) and 2C d); Charge capacities and Coulombic efficiencies measured under 60 °C at 2C e) and 4C f).

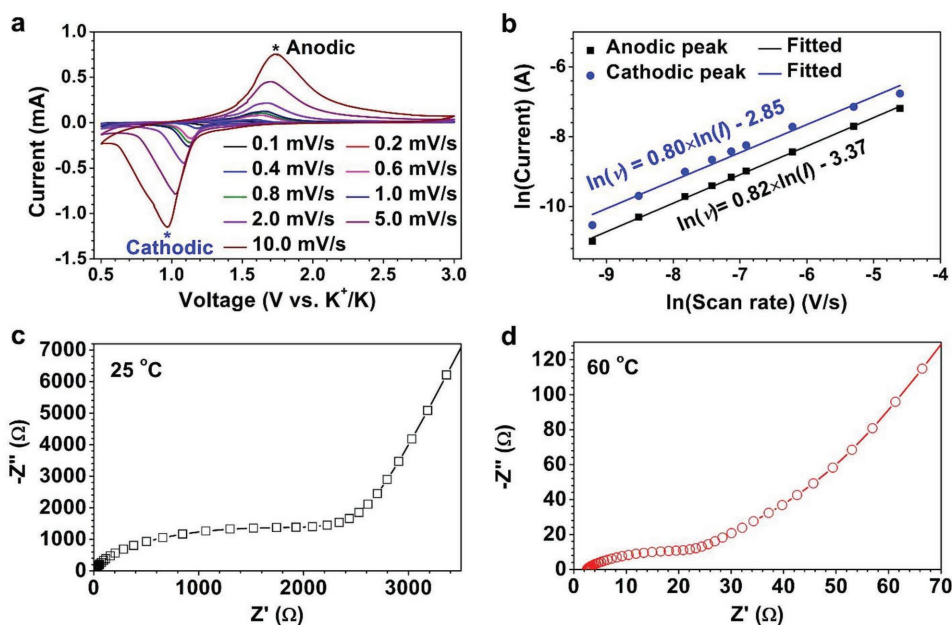


Figure 4. CV curves of ADAPTS anode at different scan rates a) and the corresponding relationship of peak currents and scan rates; b) Nyquist plots from electrochemical impedance spectroscopy (EIS) tests before cycling at 25 °C c) and 60 °C d).

high temperatures demonstrates that ADAPTS is a promising anode material for KIBs.

The mechanism for fast reaction kinetics of the ADAPTS anode was investigated by using CV at various scan rates. As shown in **Figure 4a**, the increasing scan rates result in the cathodic peaks to shift to the lower potential and the anodic peaks migrate to the higher potential, ascribing to the increased polarization.^[23,26] The peak current and scan rate were analyzed by an \ln – \ln relationship (**Figure 4b**). Linear functions are used to fit the plots. The cathodic peak exhibits a slope of 0.80 and the anodic peak displays a slope of 0.82, which is close to 1. The surface-controlled electrochemical processes exhibited a linear relationship between the peak current and the sweep rate in cyclic voltammetry at a slope close to 1.0.^[27] Thus, the fast reactions kinetics of ADAPTS anode is mainly attributed to the surface reaction. Similar surface-controlled electrochemical process in organic materials has also been observed in the fast charge/discharge polyanthraquinone cathode materials.^[28] The surface reaction mechanism also enables ADAPTS to achieve an excellent high temperature performance since the surface reaction minimizes the volume change and stabilizes the SEI even at a high temperature, which is unique for ADAPTS. In addition, the elevated temperature also accelerates the reaction kinetics, as demonstrated in the electrochemical impedance spectroscopic (EIS) of ADAPTS anode in **Figure 4c,d**. The interphase resistance represented by the depressed semicircle in **Figure 4c** is close to 2300 Ω at 25 °C, consistent with the reported observations in KIBs at the ambient temperature.^[10,29] The interphase resistance includes the solid electrolyte interphase resistance and the charge transfer resistance. The resistance tremendously decreases to ≈22 Ω at 60 °C. Moreover, the significant lower interphase resistance at high temperatures guarantees a higher capacity and better rate capability than the KIBs operated at 25 °C. The

high temperature also accelerates the diffusivity of K⁺ in the solvent. As the system is complex, the model is simplified by using Stokes–Einstein equation (Note S1, Supporting Information). The diffusion coefficient of K⁺ in the solvent at 60 °C is 1.65 times higher than that at 20 °C (**Figure S8**, Supporting Information). All the evidences confirm the better battery performance at high temperatures than that at room temperature. Galvanostatic intermittent titration technique (GITT) measurements were also performed to investigate the overpotential and equilibrium potential of ADAPTS at different charge/discharge states. As shown in **Figure S9** in the Supporting Information, the initial overpotential of ADAPTS during charge and discharge is very low (≈0.1 V). However, after charge or discharge to the capacity of ≈78 mAh g^{−1}, corresponding to half of the theoretical capacity of ADAPTS (155 mAh g^{−1}) and the reaction with one K⁺, the overpotential strikingly increases to 0.4 V for potassiation and 1 V for depotassiation. Since two K⁺ ions react with N=N in sequence via the surface reaction, the steric effect of the first K⁺ requires a high driving force for the absorption of the second K⁺ in the discharge or desorption of the first K⁺ in the charge. Thus, the GITT results further validate the reaction pathway of the ADAPTS compounds.

In conclusion, an organic compound, ADAPTS, with an azo group as the redox center to reversibly react with K⁺, provides a theoretical capacity of 155 mAh g^{−1} in K-ion batteries. The ADAPTS reacts with K-ions through a surface reaction-controlled mechanism, which ensures a high rate capability and superior high temperature performance in KIBs. At 50 °C, ADAPTS anode delivered a reversible capacity of 138 mAh g^{−1} at 1C with a capacity retention of 79% after 400 cycles. When operated at 60 °C, the ADAPTS retained a high capacity of 113 mAh g^{−1} at 2C with 81% capacity retention after 80 cycles. The extended π -conjugated structure and surface reaction mechanism in ADAPTS minimize the structural deterioration

during the rapid K^+ migration in the electrode and guarantee a superior electrochemical performance at high temperatures. This work provides a new strategy to design high-temperature KIBs with low cost and high-performance organic electrode materials.

Experimental Section

Material Synthesis: Azobenzene-4,4'-dicarboxylic acid was prepared based on the synthetic route in literature.^[30] ADAPTS were prepared as follows: Azobenzene-4,4'-dicarboxylic acid was dispersed in ethanol alcohol with potassium hydroxide powders in 5% excess. The solution was stirred at room temperature for 24 h, and then the solution was filtered to collect the precipitation. The precipitations (ADAPTS) were washed with ethanol and dried in the vacuum oven at 100 °C overnight.

Characterizations: D₂O was used as the solvent when ADAPTS were being screened by NMR and mass spectrometry. The morphology of ADAPTS was observed by SEM (HITACHI SU-70). The structure and EELS were recorded by TEM (JEOL 2100F field emission gun) with a Gatan image filter (GIF, Tridiem 863). The crystallographic information was acquired by XRD (Bruker D8 Advance). The surface elemental detection was performed by XPS (Kratos Axis 165). XPS signals were analyzed by CASA software with Shirley background. A Horiba Jobin Yvon LabRAM Raman microscope with a 532 nm laser was used to acquire Raman spectra.

Electrochemical Measurements: ADAPTS powder was mixed with carbon black and sodium alginate with a weight ratio of 6:3:1 to form a slurry that was then casted on copper foil by a doctor blade. Sodium alginate, a hydroxyl-rich binder, was used to accommodate the volume change during charge/discharge.^[31] Then the foil was dried in vacuum at 80 °C overnight. Circular electrodes were punched from the foil with a mass loading of $\approx 1.1 \text{ mg cm}^{-2}$. Coin cells (CR2032) were assembled in an argon-filled glove box ($<1 \text{ ppm}$ of water and oxygen). Potassium metal was cut into pieces as the counter electrode. The composition of electrolyte is 0.8 M KPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (v/v = 1:1). Whatman glass fiber was used as the separator. Electrochemical measurements were performed on Arbin Instruments (BT2000) with charge/discharge galvanostatic cycling from 3.0 to 0.5 V. The cyclic voltammograms were obtained by Gamry Reference 3000 Potentiostat/Galvanostat/ZRA with a scan rate from 0.1 to 10.0 mV s⁻¹. Impedance analysis was also obtained by the Gamry Reference 3000 Potentiostat/Galvanostat/ZRA. A muffle furnace was used to heat the coin cells to the target temperatures during the electrochemical tests.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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