Aqueous-Regulated Deep Eutectic Solvents for Sustainable Closed-Loop Recycling of Spent Lithium Cobalt Oxide

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Experimental Section

Preparation of Deep Eutectic Solvent: The deep eutectic solvent (DES) was prepared using choline chloride (ChCl) as the hydrogen bond acceptor and tannic acid (TA) as the hydrogen bond donor. Vacuum-dried TA and ChCl solids were weighed at a molar ratio of 1:20 and mixed thoroughly in a flask. The flask was then placed in an oil bath and stirred at 70 °C for 2 hours. To decrease the viscosity of the DES, water was added to the system to adjust the water content to 40%. After cooling to room temperature, a transparent liquid was obtained, denoted as the H_2O-modified deep eutectic solvent with 40% water content (ChCl-TA-H_2O). This ChCl-TA-H_2O was used for the leaching of spent $LiCoO_2$ (LCO) powder.

Leaching experiment: Spent LCO powder was added to 10 mL of ChCl-TA-H_2O. The mixture was stirred at 50 °C for 3 h and then naturally cooled to room temperature to yield a metal ion-rich leachate. Subsequently, cobalt ions were precipitated as cobalt tannate complexes (TA-Co) upon addition of an appropriate amount of H_2O. The mixed system was centrifuged at 8000 r/min for 5 min. The collected solids were washed three times with deionized water and dried at 70 °C for 12 h to obtain TA-Co powder.

Regeneration of DES: After each cycle, H_2O is evaporated, and a certain amount of fresh TA is supplemented to reach the original solid mass, and then H_2O is added to maintain the original viscosity. The mixture could then be gently stirred at 70 °C to restore a homogeneous state.

Preparation of Co@C: for comparison, CoC_2O_4 was first prepared as follows: $CoCl_2 \cdot 6H_2O$ (1.2 g) was dissolved in deionized water to obtain 10 mL of solution,

which was then mixed with 10 mL of 0.5 mol/L oxalic acid solution under stirring. The resulting cobalt oxalate precipitate was washed with deionized water and dried at 70 °C to yield CoC_2O_4. The dried TA-Co powder was calcined in a tube furnace at 800 °C for 3 h under a nitrogen atmosphere to yield cobalt@carbon (Co@C) for subsequent electrochemical tests.

Electrochemical measurements: For the oxygen evolution reaction (OER), 5 mg of catalyst was weighed and dispersed in a mixed solvent consisting of 750 μL of isopropanol and 50 μL of 5 wt % Nafion solution. The catalyst slurry was prepared by ultrasonication for 20 min. A piece of carbon paper (1 × 1.1 cm^2) was clamped, and 40 μL of the slurry was uniformly drop-cast onto the unclamped region (1 × 1 cm^2). After natural drying, a self-supporting electrode with carbon paper as the substrate was obtained. All electrochemical measurements were performed at room temperature using a CHI760E electrochemical workstation (Shanghai Chenhua) with a standard three-electrode system. The working electrode was the as-prepared self-supporting electrode, the reference electrode was Hg/HgO (model R0501), the counter electrode was a platinum plate, and the alkaline electrolyte was 1.0 M KOH solution. Unless otherwise stated, all potentials in this work were calibrated to the reversible hydrogen electrode (RHE) according to the following equation:

$$E\ (vs.\ RHE) = E\ (vs.\ Hg/HgO) + 0.098V + 0.059 \times pH$$

with automatic iR compensation. The OER overpotential was calculated as:

$$\eta = E(vs.\ RHE) - 1.23\ V$$

Before the test, the working electrode was activated by cyclic voltammetry (CV) at a scan rate of 10 mV s^{-1} within the test potential range until a stable state was achieved.

Material characterization: Metal concentrations are measured by an inductively coupled plasma -emission spectrometer (ICP-OES, PQ9000, AnalytikJena AG, Germany). Its morphology was characterized by scanning electron microscopy (SEM, SU8010, Hitachi, Japan). The chemical states of the elements are analyzed by

X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher, America). The crystal structure was characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). Changes in the functional groups of the samples were detected by FTIR spectroscopy (Thermo Scientific Nicoliset 10, USA). CHI 760 e electrochemical workstation (Chenhua, China) was used for electrochemical correlation test.

DFT calculations

All DFT calculations were carried out using ORCA (version: 6.1.0). [F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 73-78.] [F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, 8, e1327.] [F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2022, 12, e1606.]. Geometry optimization was conducted at the B3LYP/def2-SVP level of theory, which were dispersion corrected by D3BJ [F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.] [S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.] [J Comput Chem. 2011;32:1456–1465]. The solvent effect was evaluated by the CPCM solvation model. The RIJCOSX approximation was applied with the def2/J auxiliary basis set [Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Chem. Phys. 2009, 356, 98-109.] [Weigend, F. Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.]. The diffusion function was considered when anion was present in the system. Electrostatic potential (ESP) and independent gradient model based on Hirshfeld partition (IGMH) were analyzed with MULTIWFN [T. Lu, F. W. Chen, J. Comput. Chem. 2012, 33, 580-592] [Tian Lu, J. Chem. Phys., 161, 082503 (2024)]; and the results were visualized with VMD software [W. Humphrey, A. Dalke and K. Schulten, J. Mol. Graph., 1996, 14, 33-38].

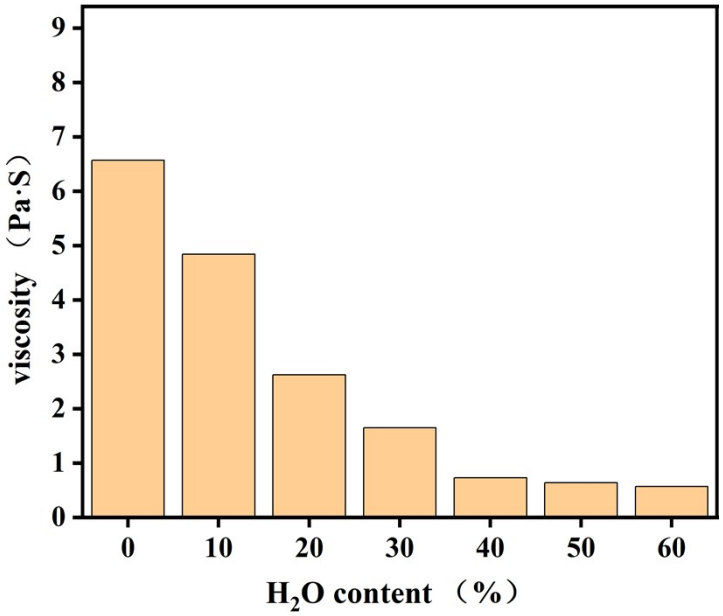

Figure S1 Viscosity of ChCl-TA with different H_2O content

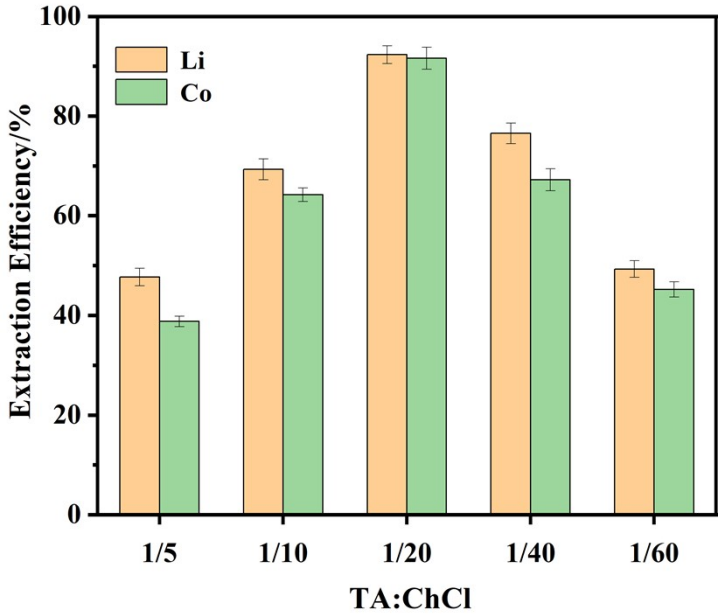

Figure S2 Effect of TA:ChCl molar ratio on the leaching efficiencies of metal ions.

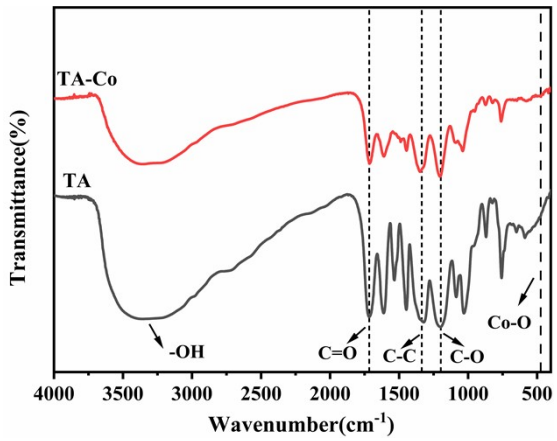

Figure S3 FT-IR spectra of TA and TA-Co

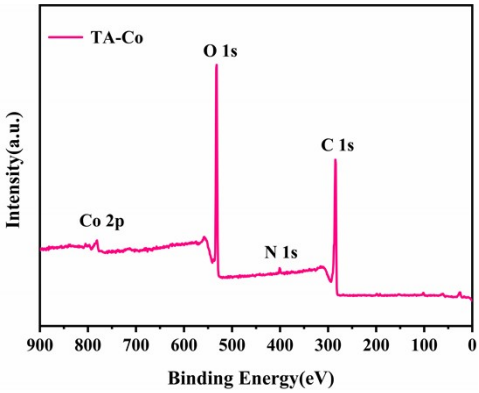

Figure S4 XPS spectrum of TA-Co

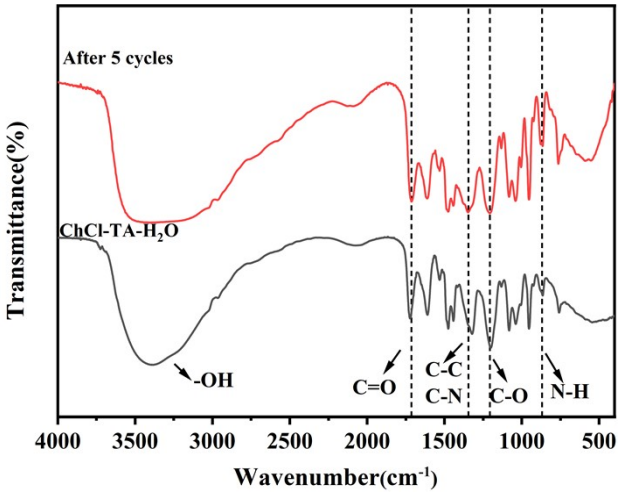

Figure S5 FT-IR spectra of DES after 5 cycles

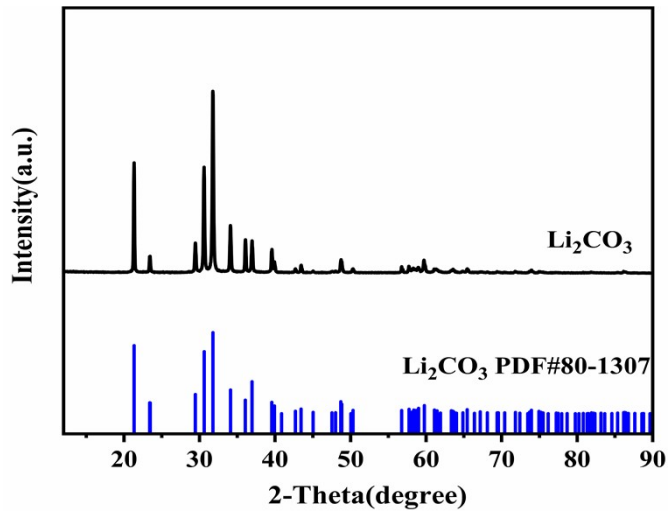

Figure S6 XRD pattern of Li_2CO_3

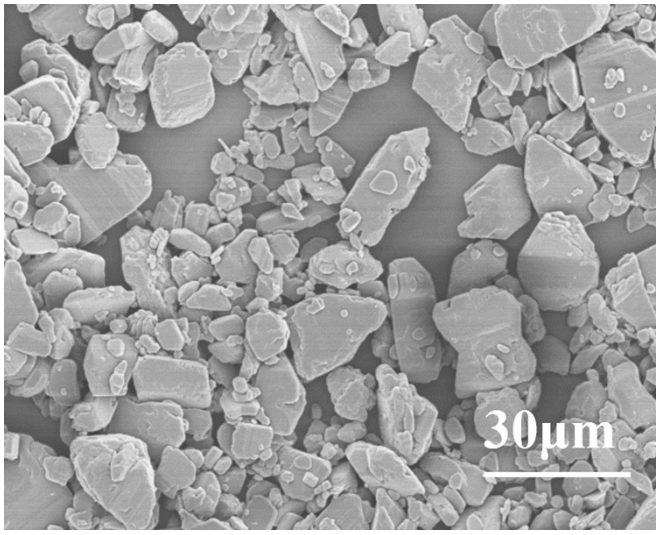

Figure S7 XPS of Li_2CO_3

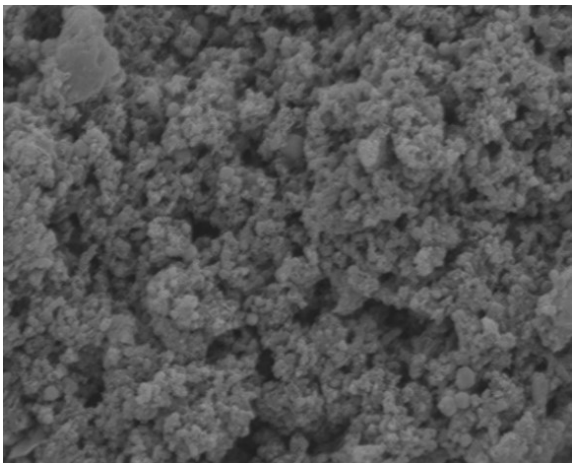

Figure S8 SEM iamge of Co@C

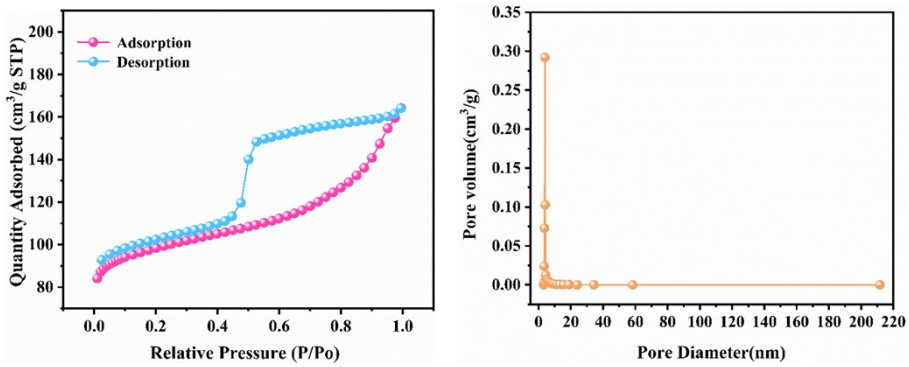

Figure S9 N_2 adsorption-desorption isotherm and pore size distribution of Co@C