

Supporting Information for

MOF derived composites for cathode protection: coatings of LiCoO₂ from UiO-66 and MIL-53 as ultra-stable cathodes

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Experimental section

The synthesis of UiO-66 were carried out under mild hydrothermal conditions using zirconium tetrachloride (ZrCl₄, 2.330 g), 1,4-benzenedicarboxylic acid (C₆H₄-1,4-(CO₂H)₂ or BDC, 1.661 g), and dimethylformamide (DMF, 30 mL). The reaction was performed in a 100 mL Teflon-lined stainless steel Parr bomb under autogenous pressure for 24 h at 220 °C.

The synthesis of MIL-53 were carried out under mild hydrothermal conditions using aluminum nitrate nonahydrate (Al(NO₃)₃ · 9H₂O, 1.300 g), 1,4-benzenedicarboxylic acid (C₆H₄-1,4-(CO₂H)₂ or BDC, 0.288 g), and deionized water (80 mL). The reaction was performed in a 100 mL Teflon-lined stainless steel Parr bomb under autogenous pressure for 72 h at 220 °C.

UiO-66@LiCoO₂ and MIL-53@LiCoO₂ were both synthesized through a simple mechanochemical synthetic protocol. Reactions were carried out

in a ball mill (QM-3B, Nanjing University Instrument Factory, China) using a 80 mL PTFE grinding jar with five 10 mm zirconia balls. A solid mixture of LiCoO_2 (2.000 g), UiO-66 (0.220 g) (or MIL-53 (0.060 g)) and ethanol (400 μL) was placed into the jar and ground at high speed for 1h.

The as-prepared UiO-66@LiCoO_2 (or MIL-53@LiCoO_2) were transferred to a tube furnace and were annealed at 600 °C for 5 h in air under constant heating and cooling rates of 5 °C min^{-1} . After that, the as-prepared product was transferred to the grinding jar with five 10 mm zirconia balls and ground at high speed for 1h, followed by another heating treatment at 500 °C of 4 h in air under the same heating and cooling rates.

$\text{ZrO}_2\text{@LiCoO}_2$ and $\text{Al}_2\text{O}_3\text{@LiCoO}_2$ were both conducted in a similar fashion through a simple mechanochemical synthetic protocol by treating commercial LiCoO_2 (2.000 g) with ZrO_2 (0.030 g, PDF # 65-1022) or Al_2O_3 (0.070 g, PDF # 46-1212) powders. The powders were placed into the jar and ground at high speed for 1h. The as-prepared $\text{ZrO}_2\text{@LiCoO}_2$ (or $\text{Al}_2\text{O}_3\text{@LiCoO}_2$) were transferred to a tube furnace and annealed at 600 °C for 5 h) in air under constant heating and cooling rates of 5 °C min^{-1} .

Characterization

Powder X-ray diffraction (PXRD) was conducted with monochromatized

Cu-K α ($\lambda = 1.54178 \text{ \AA}$) incident radiation on a D8 Advance Bruker powder diffractometer operating at 40 kV and 50 mA. Nitrogen sorption isotherm was measured at 77 K on a Quantachrome Instrument Autosorb-IQ7 after pretreatment by heating the samples under vacuum at 180 °C for 3 h before the measurement. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker ALPHA FT-IR Spectrometer. ICP (Inductive Coupled Plasma Emission Spectrometer) was tested by Varian 725 inductively coupled plasma emission spectrometer. Scanning electron microscopic (SEM) images were obtained with a JEOL JSM7500F instrument.

To prepare the cathodes, 86 wt% active material, 8 wt% Super P carbon black and 6 wt% poly(vinylidene fluoride) (PVDF) binder were mixed in N-methyl pyrrolidinone (NMP) to form a slurry. The slurry was cast onto aluminium foil and dried under vacuum at 120 °C for 12 h. The loading mass of active material is about 2.45 mg/cm². Coin cells of CR2032 type were assembled in an argon-filled glove box using a lithium metal anode and a polypropylene microporous separator (Celgard 2400). The electrolyte was 1 M LiPF₆ in ethyl carbonate (EC), methyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 v/v/v). The coin cells were allowed to be aged overnight before tested. Galvanostatic tests were carried out between 3.0 V and 4.5 V with a LAND CT2001A instrument (Wuhan, China) at ambient temperature (or 55 °C). The electrochemical

impedance spectra were also performed using an electrochemical workstation (CHI 760E: CH Instrumental Inc.) with the frequency range of 10^4 Hz to 10^{-1} Hz with an applied voltage of 4.5 V after 4 cycles at current density of 77.5 mA g^{-1} .

The active material in all the cells is the sum of LiCoO_2 and coating layer.

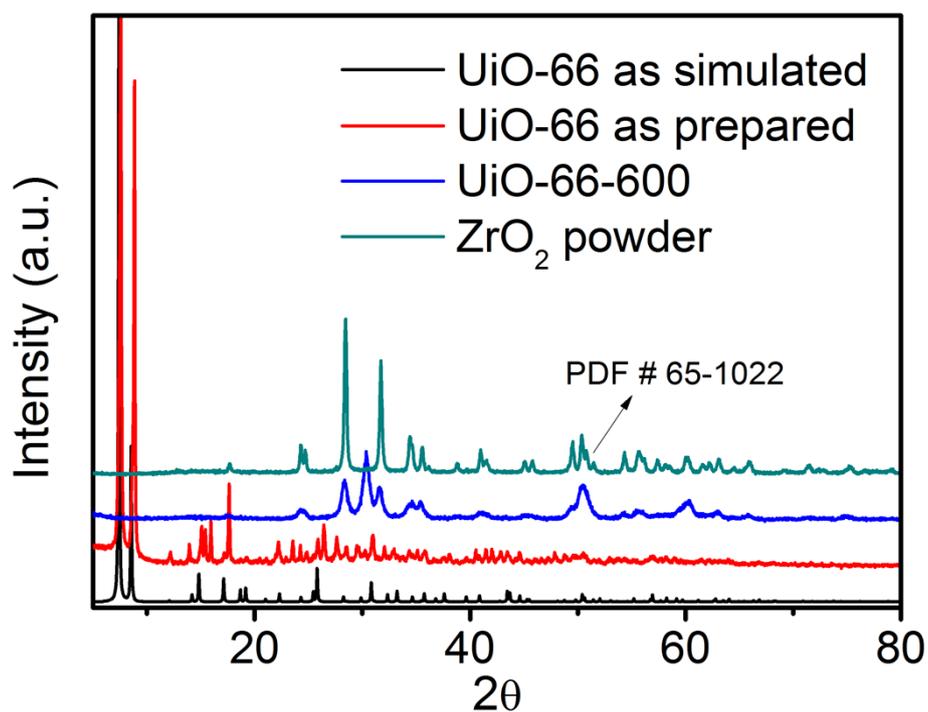


Fig. S1 PXRD of UiO-66, UiO-66-600 and ZrO_2 .

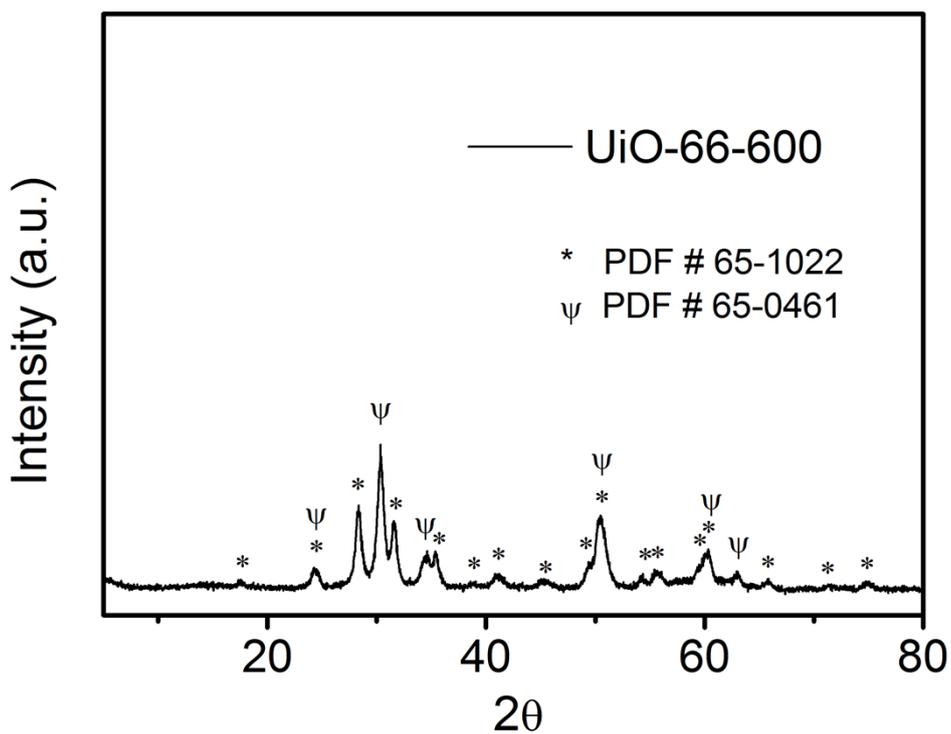


Fig. S2 PXRD UiO-66-600.

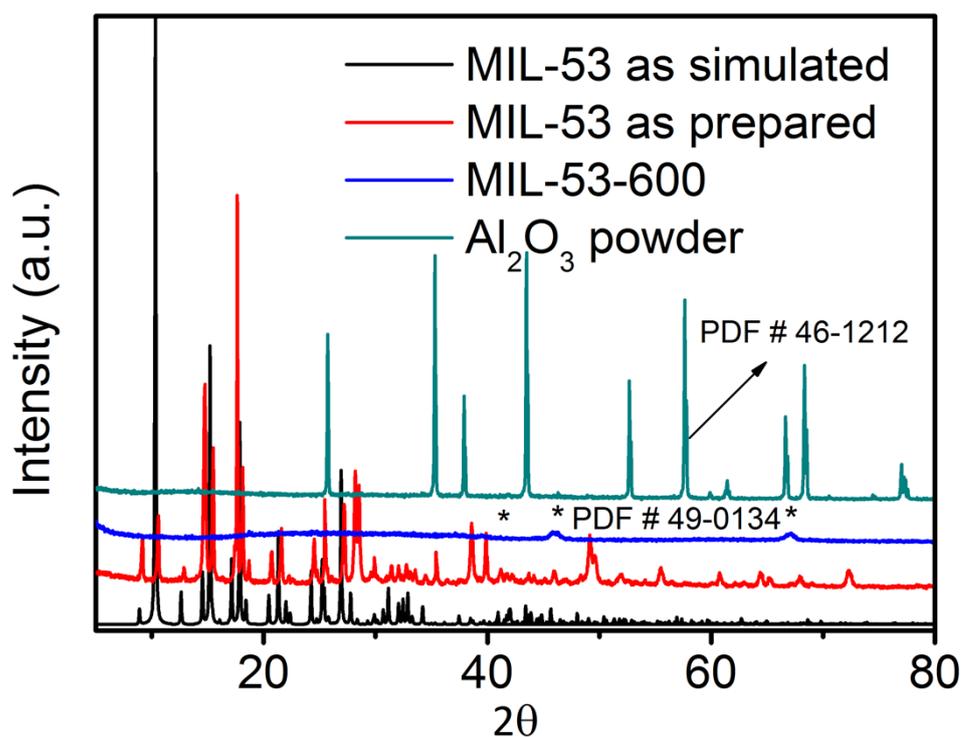


Fig. S3 PXRD of MIL-53, MIL-53-600 and Al_2O_3 .

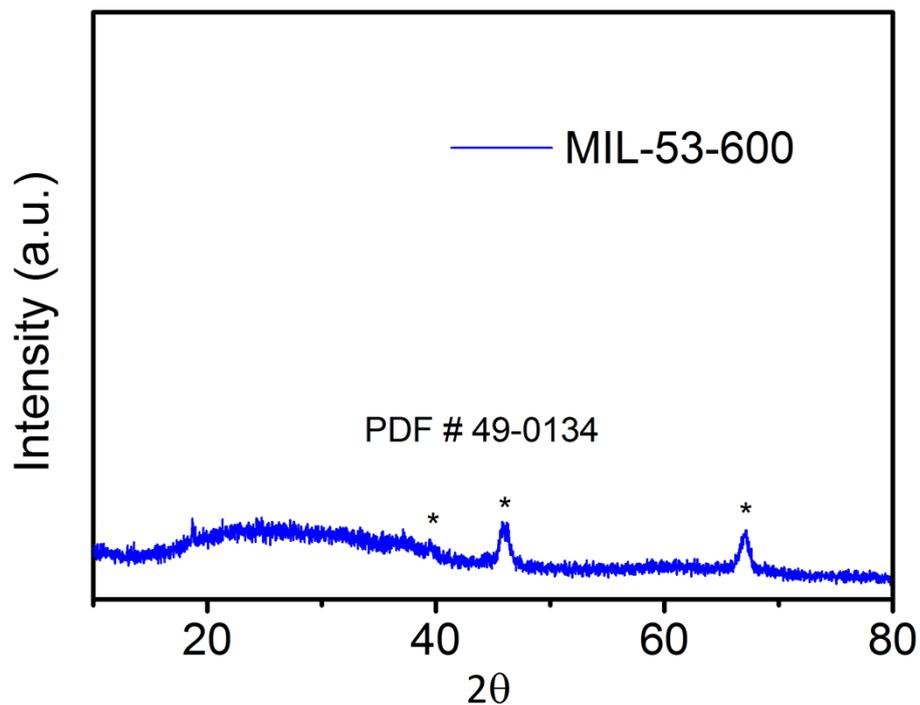


Fig. S4 PXRD of MIL-53-600.

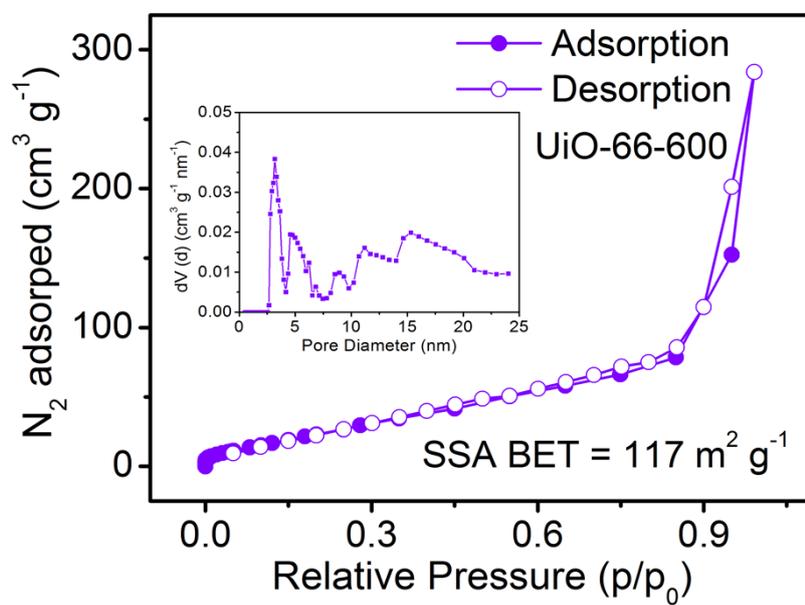


Fig. S5 Nitrogen adsorption isotherms at 77 K for UiO-66-600. Inset shows the pore size distribution from DFT calculation.

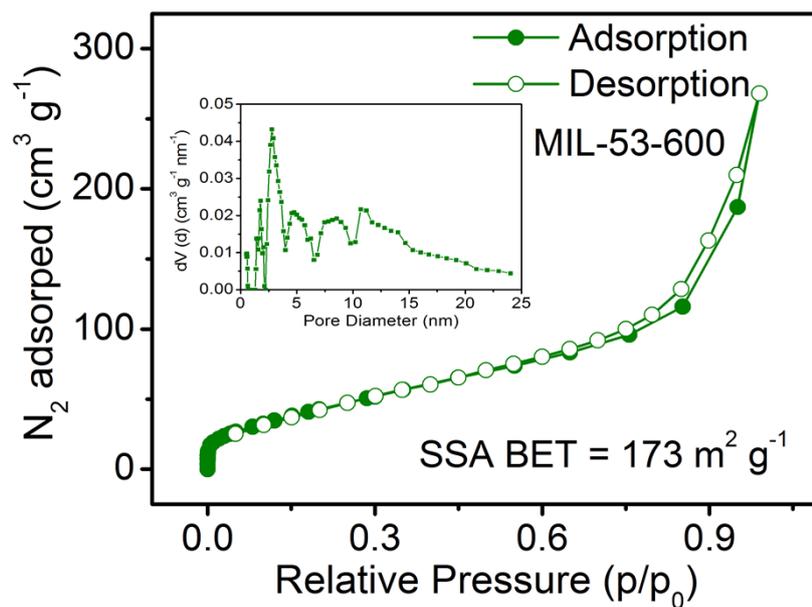


Fig. S6 Nitrogen adsorption isotherms at 77 K for MIL-53-600. Inset shows the pore size distribution from DFT calculation.

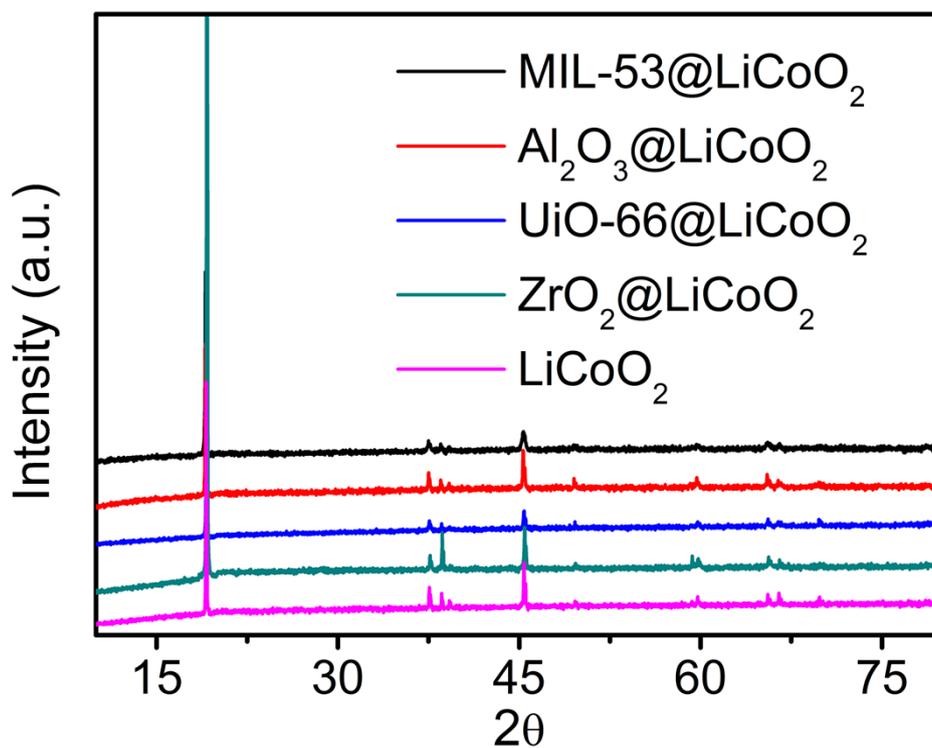


Fig. S7 PXRD of MIL-53@LiCoO₂, Al₂O₃@LiCoO₂, UiO-66@LiCoO₂, ZrO₂@LiCoO₂ and LiCoO₂.

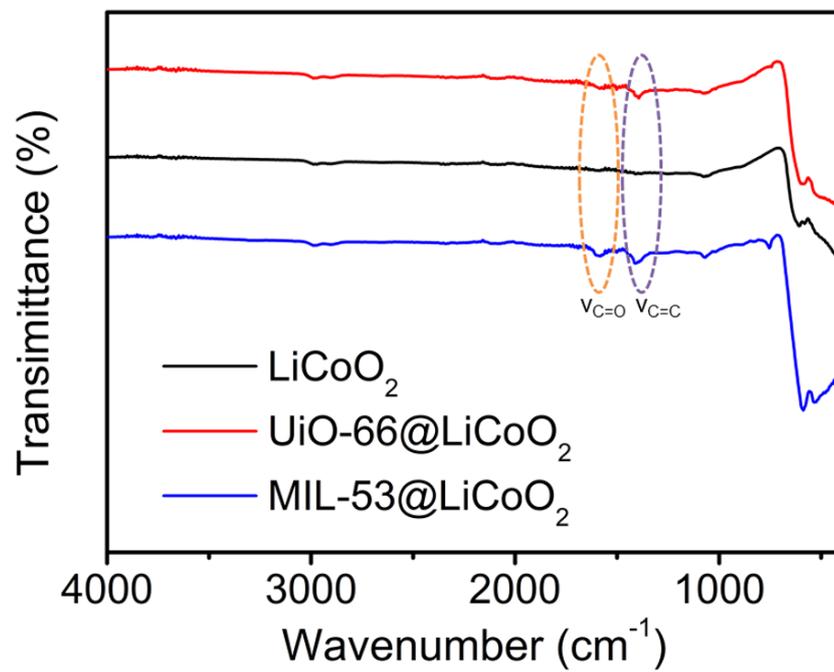


Fig. S8 FT-IR of the LiCoO_2 , UiO-66@LiCoO_2 and MIL-53@LiCoO_2 .

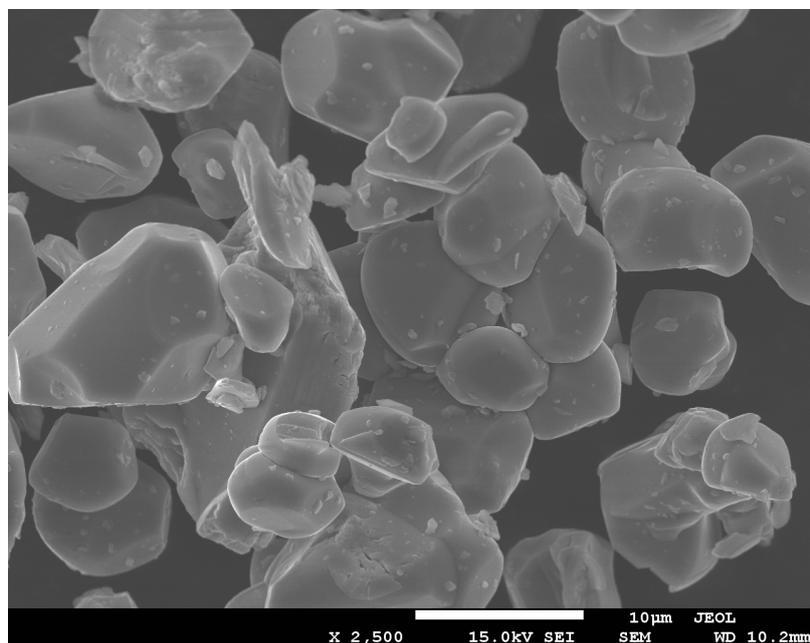


Fig. S9 SEM image of LiCoO_2 .

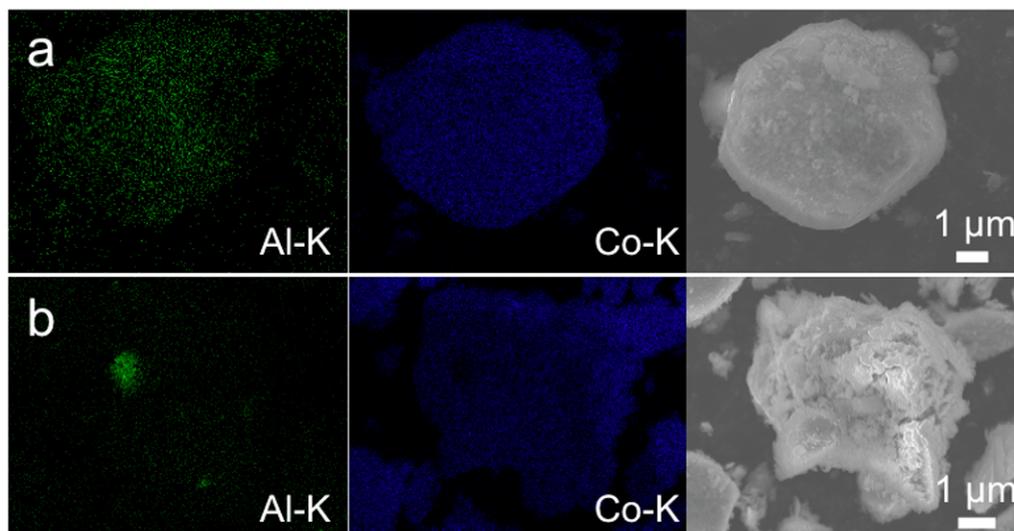


Fig. S10 (a) SEM images and elemental mapping of (a) MIL-53@LiCoO₂-600, (b) Al₂O₃@LiCoO₂-600 (green dots: Al, blue dots: Co).

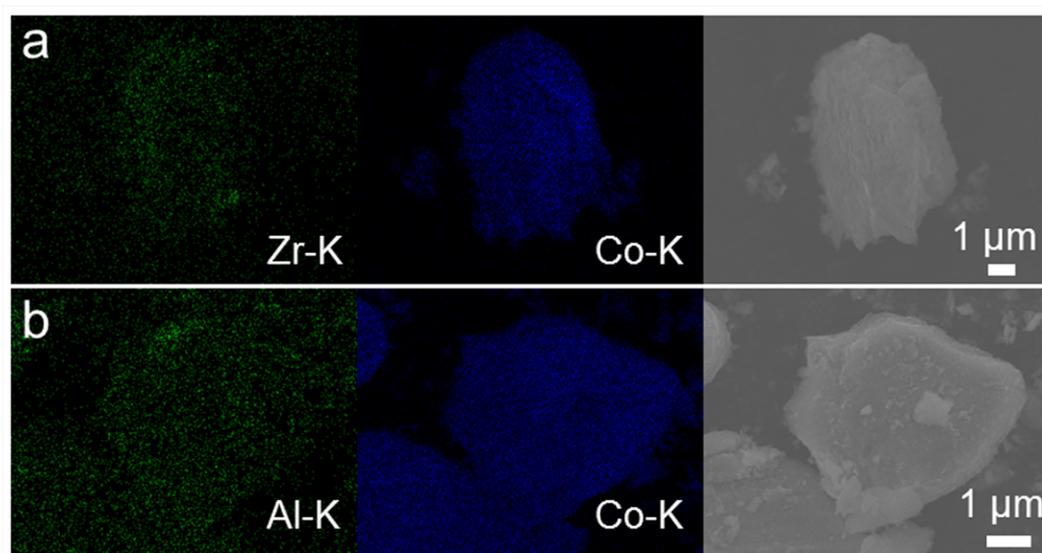


Fig. S11 (a) SEM images and elemental mapping of (a) UiO-66@LiCoO₂-600, (b) MIL-53@LiCoO₂-600 (green dots: Zr (or Al), blue dots: Co).

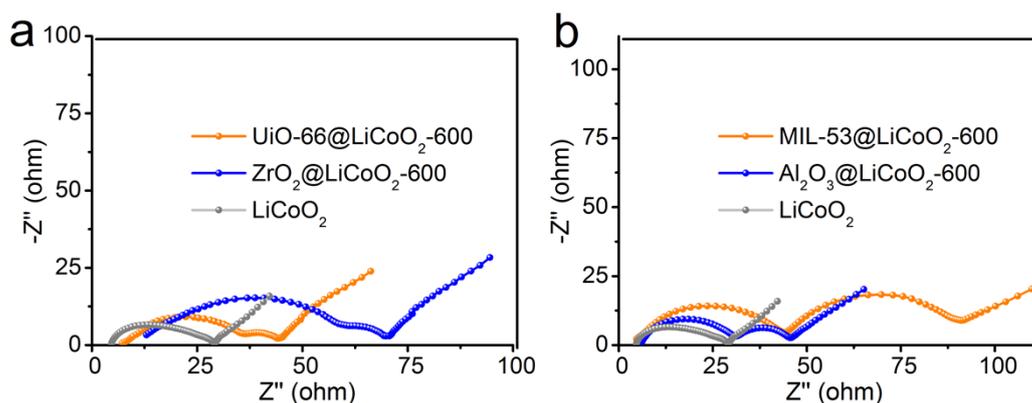


Fig. S12 Nyquist plots for (a) UiO-66@LiCoO₂-600, ZrO₂@LiCoO₂-600, (b) MIL-53@LiCoO₂-600, Al₂O₃@LiCoO₂-600 and LiCoO₂ after four cycles.

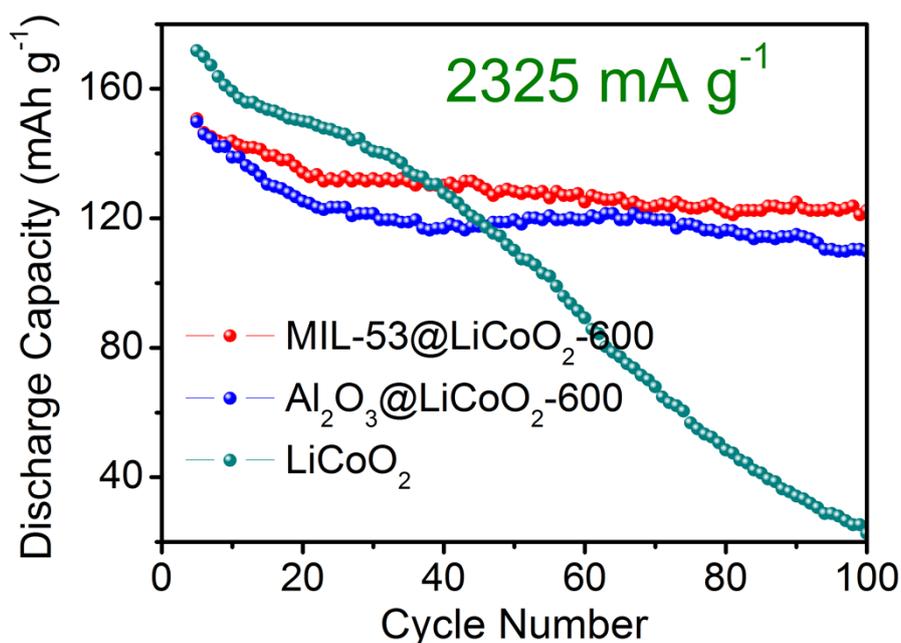


Fig. S13 Cycle-life performance of MIL-53@LiCoO₂ between 3.0 and 4.5 V at a current density of 2325 mA g⁻¹ at room temperature, the cell was activated at a current density of 77.5 mA g⁻¹ for the first four cycles.

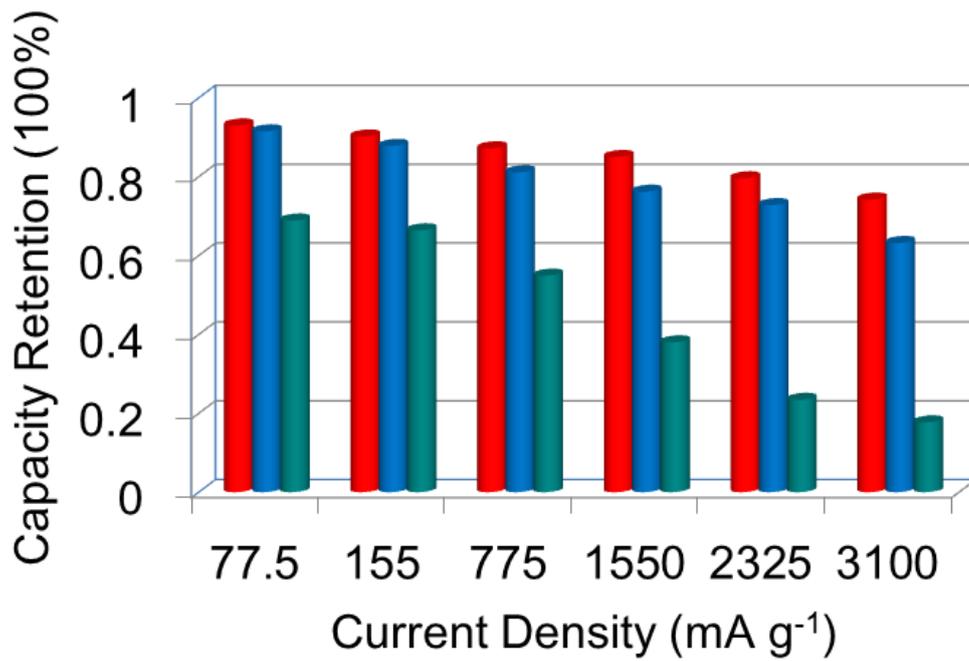


Fig. S14 Capacity retention for LiCoO₂ (dark cyan line), Al₂O₃@LiCoO₂-600 (blue bar) and MIL-53@LiCoO₂-600 (red bar).

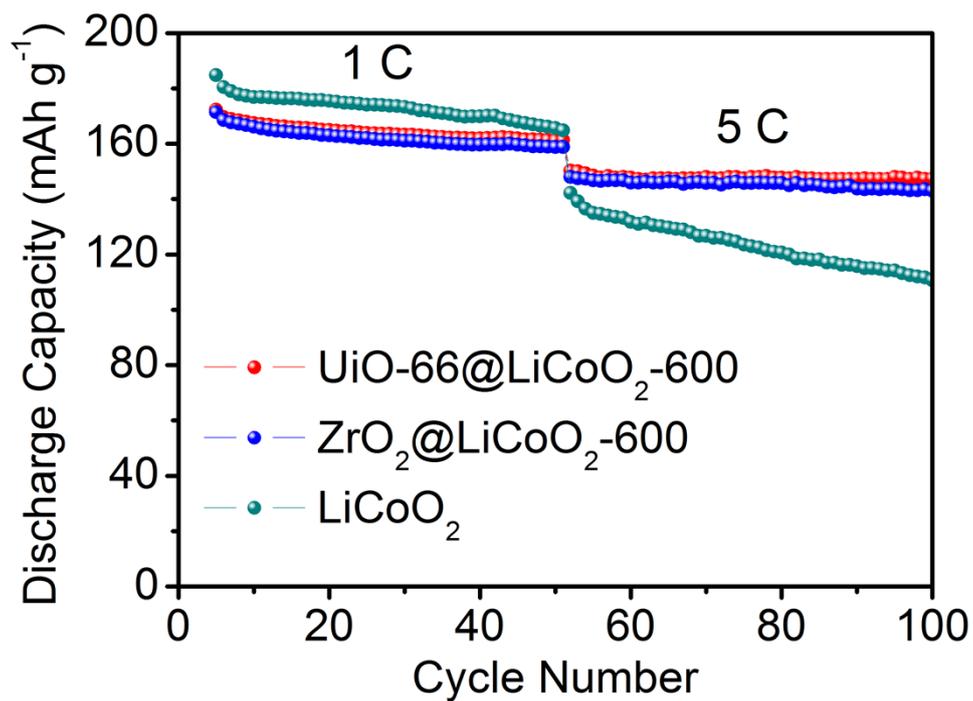


Fig. S15 Cycle-life performance of UiO-66@LiCoO₂-600, ZrO₂@LiCoO₂-600 and LiCoO₂ between 3.0 and 4.5 V at rate of 1 C and 5 C (1 C = 180 mA g⁻¹) at room temperature; the cell was activated at a rate of 0.5 C for the first four cycles.

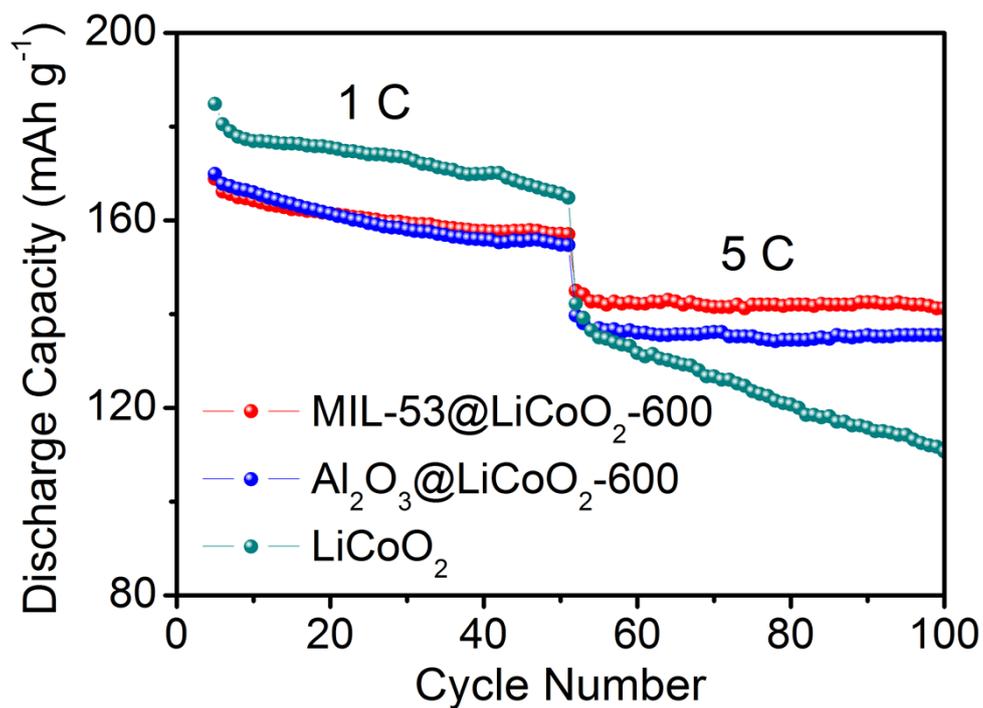


Fig. S16 Cycle-life performance of MIL-53@LiCoO₂-600, Al₂O₃@LiCoO₂-600 and LiCoO₂ between 3.0 and 4.5 V at rate of 1 C and 5 C (1 C = 180 mA g⁻¹) at room temperature; the cell was activated at a rate of 0.5 C for the first four cycles.