A Reversible and Stable Flake-like $LiCoO_2$ Cathode for Lithium Ion Batteries

Tao Wei[1,2], *Rui Zeng*[2], *Yongming Sun*[2], *Yunhui Huang*[2,*], *and Kevin Huang*[1,*]

[1]Department of Mechanical Engineering,

University of South Carolina, Columbia, SC29208, USA. E-mail: kevin.huang@sc.edu

[2]State Key Laboratory of Material Processing and Die and Mold Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China. E-mail: huangyh@hust.edu.cn

Experiment Section

The micro-sized flake-like $LiCoO_2$ cathode was synthesized with a two-step method. CoO nanoplates served as the precursor to form $LiCoO_2$. CoO nanodisks were synthesized from a wet chemical route. First, a 10 mmol of cobalt acetate tetrahydrate (2.4908g) was dissolved into a 200 mL of deionized (DI) water. Then, 5 mL of hydrazine hydrate (80 wt%) was added into the solution with 100 mL DI water as diluent under a continuous stirring for 24 h at room temperature. The as-formed precipitate was filtered, washed repeatedly with DI water and ethanol, and dried at 80 °C overnight. A hierarchical CoO nanodisks structure was finally obtained by annealing the product at 300 °C in air for 2 h. Then, as-prepared CoO nanodisks were mixed with 10% excess $LiOH \cdot H_2O$ in ethanol solution, milled gently for about 1 h to get a homogenized powder. Finally, the mixed powder was calcined in air atmosphere at 850 °C for 10 h to obtain the flake structure $LiCoO_2$. Powder X-ray diffraction (XRD) studies were carried out using a X'Pert PRO (PANalytical B.V., Holland) diffractometer with high-intensity Cu $K\alpha_1$ irradiation ($\lambda = 1.5406$ Å). XRD patterns for this flake $LiCoO_2$ was shown in Figure S1, and the XRD patterns for the normal $LiCoO_2$ synthesized by solid phase reaction was shown in Figure S2.

The morphology and microstructure of the prepared materials were characterized by scanning electron microscopy (SEM, FEI, Sirion 200) and transmission electron microscopy (TEM, JEOL 2100F).

Coin cells (CR2032) structure was used for electrochemical measurements. For electrodes fabrication, the working electrodes consisted of 80 wt% active material, 10 wt% acetylene black (used as conductive carbon black) and 10 wt% polyvinylidene fluoride (PVDF, used as polymer binder) in N-methyl-2-pyrrolidone. An aluminium foil (8 mm in diameter) was used as the current collector. The obtained slurry was coated onto Al foils and dried at 80 °C to remove the solvent. Then, the electrodes were pressed and cut into disks and further dried at 80 °C for 24 h in air atmosphere. Coin cells were assembled in an argon-protected glove box. A lithium foil was used as the counter electrode and a Celgard 2300 membrane was used as the separator. The commercial electrolyte was composed of 1 mol·L^{-1} $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (v/v = 1:1). The galvanostatic charge-discharge tests were carried out with a Land Battery measurement system (Land, China) at various current densities with a cut-off voltage of 2.5–4.4 V vs. Li/Li^+ at room temperature. For 2 C and 5 C rate testing, 0.1 C rates were first used to activate the cell for 3 cycles.

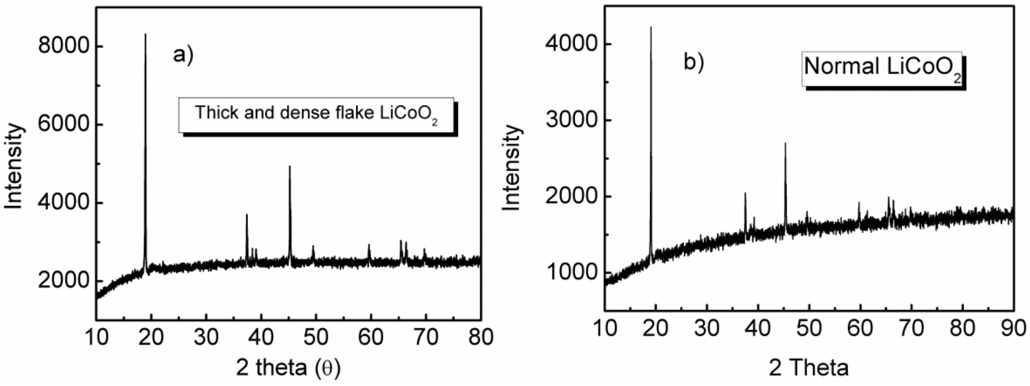

Figure S1. XRD patterns of $LiCoO_2$ powders: a) flake-like; b) normal.

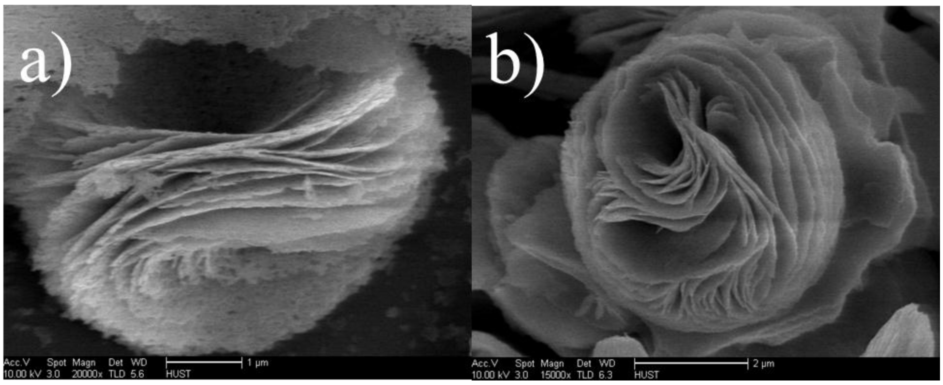

Figure S2. FESEM images of the flake-like CoO.

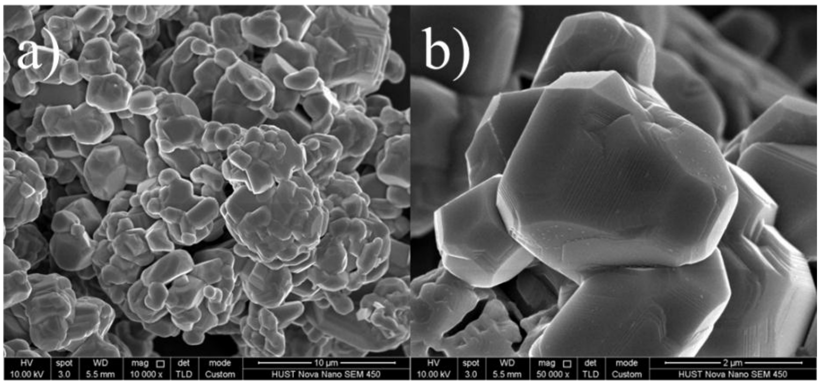

Figure S3. FESEM images of the normal (named C1) $LiCoO_2$ powder sintered at 850°C for 10h.

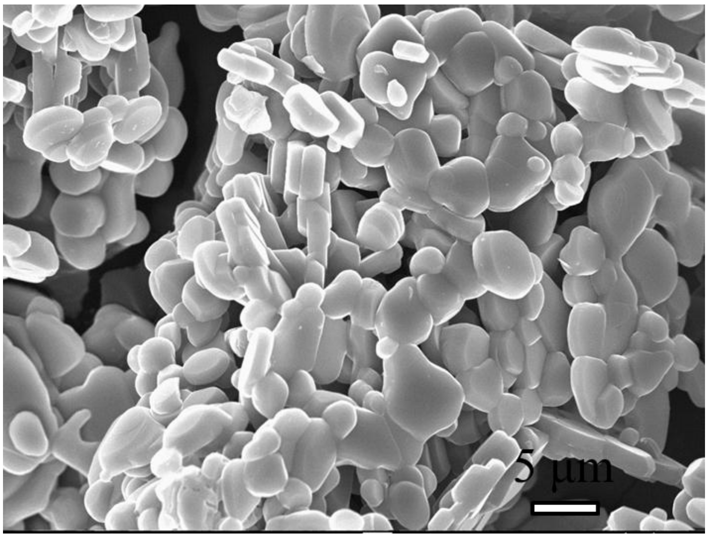

Figure S4. The lower magnification SEM image of the dense and thick $LiCoO_2$ flakes.

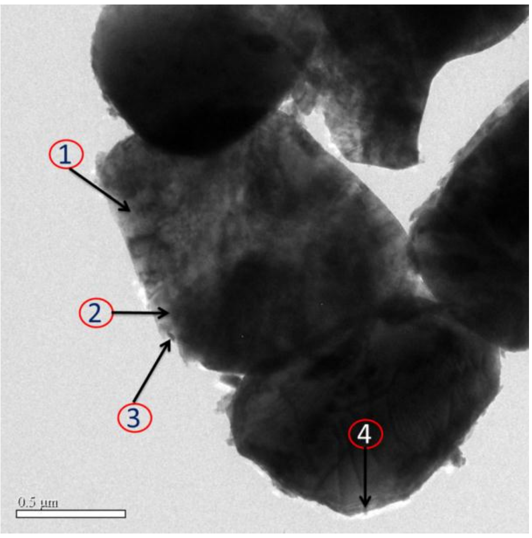

Figure S5. TEM image of the original flake-like $LiCoO_2$. The corresponding SAED patterns of the labeled areas are shown Figure S6.

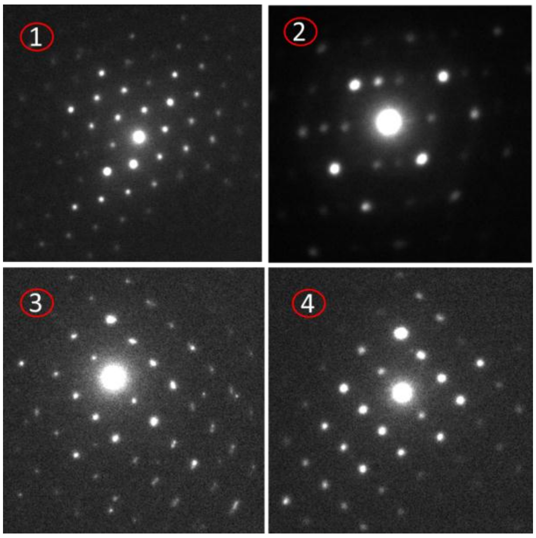

Figure S6. SAED patterns showing exposed (001) plane in the labeled areas 1 and 2 and the straight side edges (100) and (010) planes in the label areas 3 and 4 of the flake-like $LiCoO_2$ shown in Figure S5.

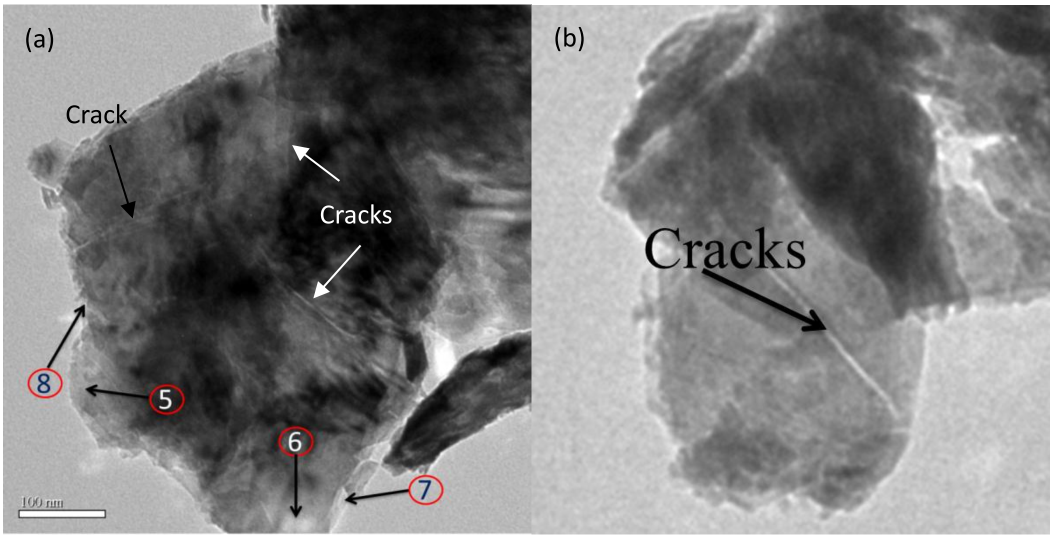

Figure S7. (a) TEM image of the flake-like $LiCoO_2$ after 100 cycles. The corresponding SAED pattern from the labeled areas 5, 6, 7, and 8 are shown Figure S8. Some visible micro-cracks are visible; (b) an enlarged view of cracks

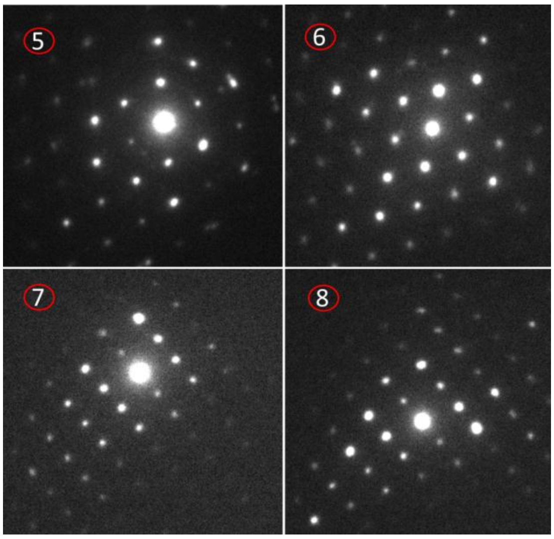

Figure S8. SAED patterns showing exposed (001) plane in the labeled areas 5 and 6 and the straight side edges (100) and (010) planes in the label areas 7 and 8 of the flake-like $LiCoO_2$ after 100 cycles.

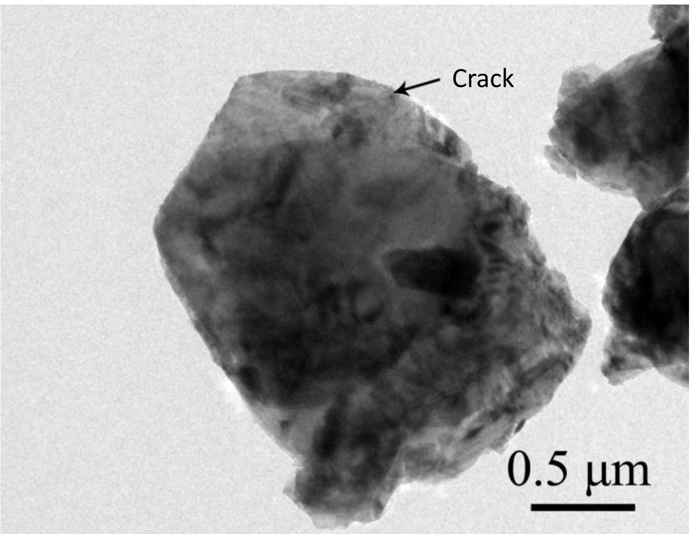

Figure S9. TEM image of flake-like $LiCoO_2$ after 3 cycles with visible micro-cracks.

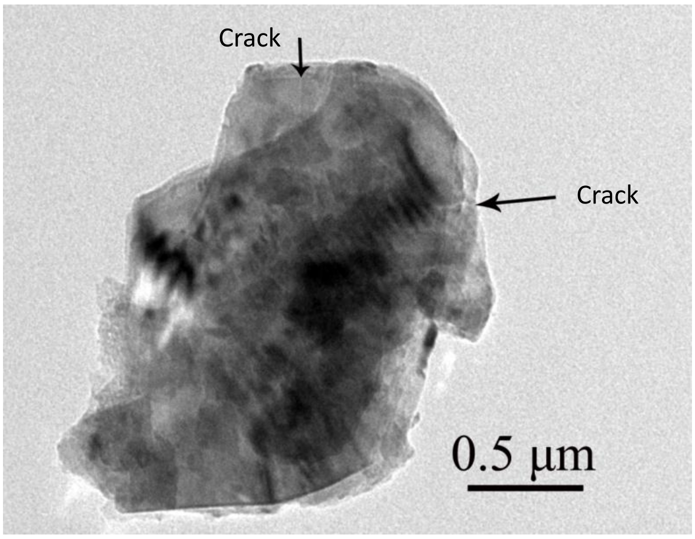

Figure S10. TEM image of flake-like $LiCoO_2$ after 100 cycles with visible micro-cracks.

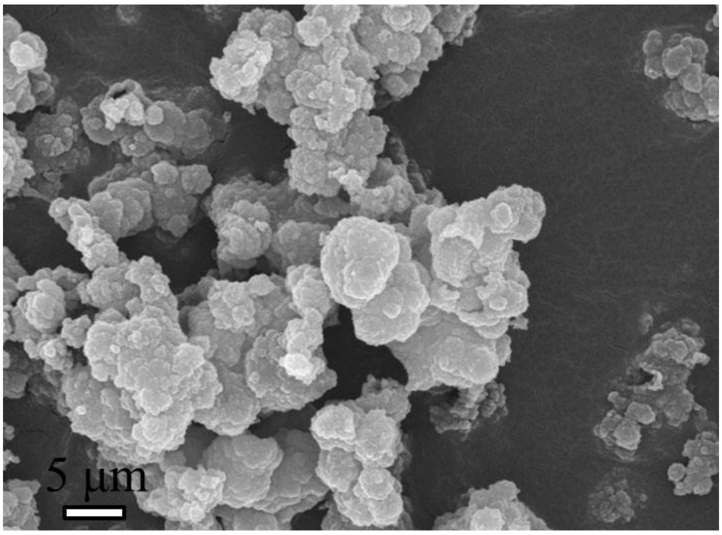

Figure S11. FESEM image of $LiCoO_2$ synthesized from the CoO nanoplates and $LiNO_3$ precursor sintered at 850°C for 10h.

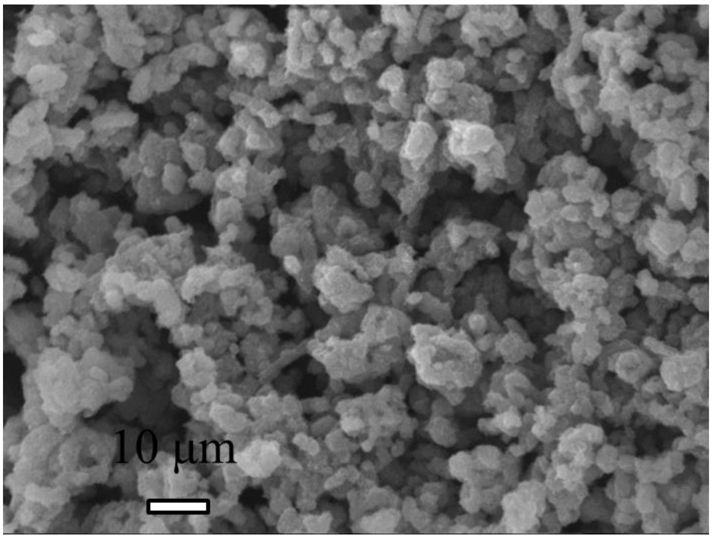

Figure S12. FESEM image of $LiCoO_2$ synthesized with a Sol-Gel method and sintered at 850^{o}C for 10h.