

Supplementary Information

for

Dopants Modulate Crystal Growth in Molten Salts Enabled by Surface Energy Tuning

Xiaoqiao Li,^{1, 2, †} Linming Zhou,^{3, †} Han Wang,² Dechao Meng,² Guannan Qian,² Yong Wang,² Yushi He,² Yongjun Wu,³ Zijian Hong,^{3,*} Zi-Feng Ma,² Linsen Li^{2, 4, *}

¹ College of Environmental & Chemical Engineering, Shanghai University of Electric Power; Shanghai 200090, China

² Department of Chemical Engineering, Shanghai Jiao Tong University; Shanghai 200240, China

³ School of Materials Science & Engineering, Zhejiang University; Hangzhou 310027, China

⁴ Shanghai Jiao Tong University Sichuan Research Institute, Chengdu 610213, China

† These authors contributed equally to this work.

*Corresponding authors: Zijian Hong (hongzijian100@zju.edu.cn) and Linsen Li (linsenli@sjtu.edu.cn)

Methods

Material synthesis

The LiCoO₂ samples were synthesized in LiOH-Li₂SO₄ molten salts using Co₃O₄ as the cobalt source. In a typical experiment, 0.0033 mole of Co₃O₄, 0.015 mole of LiOH, and 0.002 mole of Li₂SO₄ were manually mixed in an agate mortar and then transferred to an alumina crucible. The powders were heated to 910 °C in air at a ramping rate of ~10 °C min⁻¹ and then kept at 910 °C for 10 h. During cooling, the powders were slowly cooled down to 300 °C at a rate of 2 °C min⁻¹ and then naturally cooled to room temperature. The LiCoO₂ samples were separated from the salts by water washing and sonication and dried in an oven at 60 °C. In the doping experiments, a certain amount of dopant was mixed with Co₃O₄, LiOH, and Li₂SO₄ initially while all the other experimental procedures remain the same. Mg(OH)₂, Al(OH)₃, TiO₂, Zr(OH)₄, Nb₂O₅, MoO₃, and WO₃ were used as the dopants. The LiCoO₂ samples were thermally treated again at 1000 °C for 10 h before they were used for electrochemical testing.

DFT calculations

In this study, the DFT+U calculations was performed with the open source GPAW package [1, 2] using the real-space projector-augmented wave (PAW) method [3,4]. First, bulk calculation was performed with GGA level Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [5], with a real space grid spacing of 0.14 Å. Monkhorst Pack scheme was used for sampling the Brillouin zone, with 8 × 8 × 8 k -point mesh. The cutoff force for all calculations was set to below 0.01 eV Å⁻¹. The Hubbard *U* value of 2.4 is applied to the *d*-orbitals for Co, which was determined by fitting the experimental bandgap of 2.5 eV for bulk LiCoO₂ [6]. The bulk lattice constants were then calculated as *a* = 2.864 Å and *c* = 14.216 Å, close to the previous reports [6]. Then, the (0001) surface slab was built with 6 layers and a total of 216 atoms, while a vacuum of 5 Å was applied on each side of the slab. For the doped system, one Co atom on each side of the surface was substituted by a dopant atom. Whereas the (10 $\bar{1}$ 4) surface slabs were built with 4 layers and 144 atoms. The k-points were set as 4 × 4 × 1 and the convergence criterial was set to below 0.05 eV Å⁻¹ for all the surface calculations. The Hubbard *U* value was also applied to the *d* bands for some of the dopants, e.g., 4.0 for Nb [7], 4.0 for Zr [8], 2.5 for Ti [9] and 6.3 for Mo [10], respectively.

Material characterizations

PXRD measurements were carried out using a poly-functional X-Ray diffractometer powder diffraction (Bruker D8) using Cu K α radiation. SEM micrographs were taken using a Phenom Pro scanning electron microscope at an acceleration voltage of 10 kV. SEM-EDX measurements were made using a TESCAN MAGNA UHR SEM. The particle sizes distribution was measured by a particle size analyzer (Mastersizer2000). TOF-SIMS measurements were made using ION-TOF TOF-SIMS 5-100. A Bi⁺ ion beam at 30 keV and 500 pA was used as the primary ion beam to etch the samples with an analysis area of 10 × 10 μ m².

Electrochemical measurements

The LCO samples, super P carbon black, and PVDF binder were mixed in N-methyl pyrrolidone at a weight ratio of 90:5:5 to make a slurry, which was coated onto aluminum foil using a film applicator. The as-made electrodes were dried at 120 °C for 10 h under vacuum and cut into discs (10 mm in diameter) for coin cell tests. The typical loading of LCO was around

3–4 mg cm⁻². Half-cells were assembled using Li foil (450 μm in thickness) as the anode, a polyethylene separator, and 1 M LiPF₆ dissolved in EC-EMC (3/7 by weight) + 2 wt% VC as the electrolyte in an argon-filled glove-box (Mikrona, O₂/H₂O < 0.1 ppm).

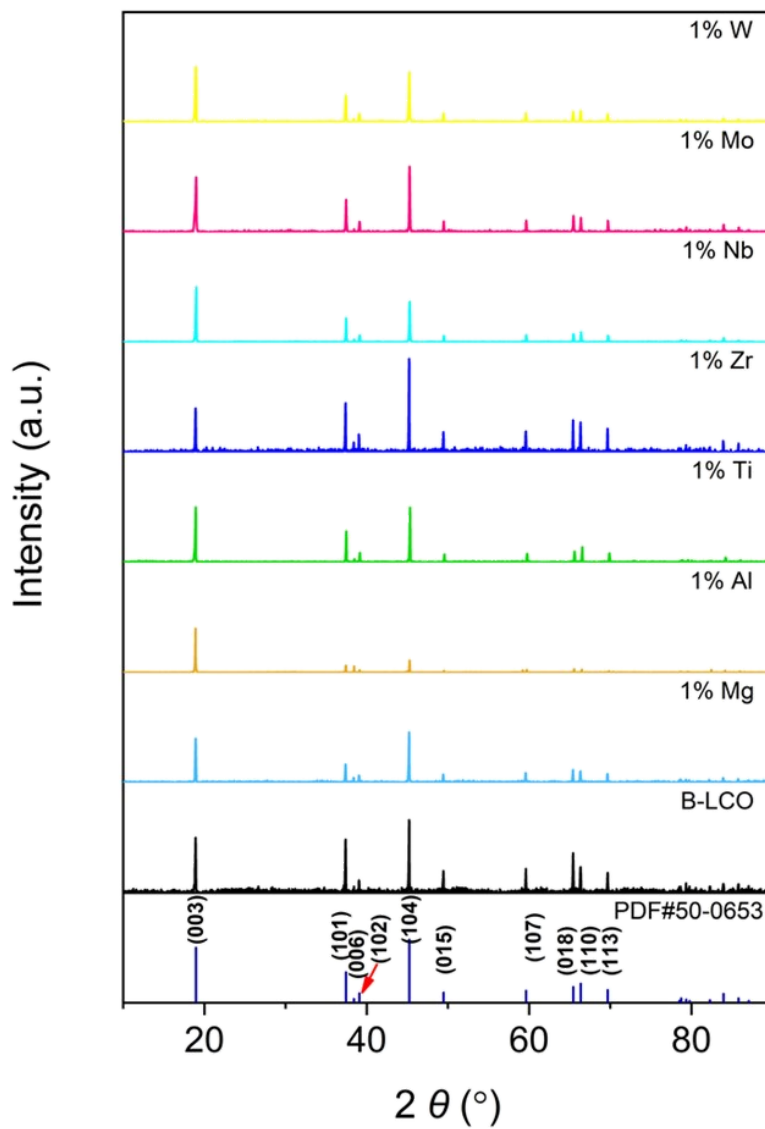
Artificial graphite (Shanshan) was used as the anode in the full cell tests. The artificial graphite powder, super P carbon black, and PVDF binder were mixed in N-methyl pyrrolidone at a weight ratio of 90:5:5 to make a slurry, which was coated onto copper foil using a film applicator. The graphite electrodes were dried at 80 °C for 10 h under vacuum. The typical loading of graphite was around 5 mg cm⁻² while the LCO cathode loading was around 9 mg cm⁻² for the full cells. The n/p ratio was ~1.08.

Electrochemical cycling measurements were performed using battery cyclers (Shenzhen Neware, BTS4000-5V) in a voltage range of 4.5-3.0 V at various C-rates. The coin cells were cycled inside temperature chambers set at 30 °C for the half cells. For the half-cell tests, the cells were first cycled at 0.1 C for three cycles, then cycled at 0.33 C. A 0.1 C cycle was applied every 20 cycles. For the full cell tests, the cells were first charged at 0.05 C to 4.4 V and then held at this voltage until the current dropped to 0.02 C. Next, the cells were discharged at 0.05 C to 2.9 V. The long-term cycling was carried out at 1 C. The rate capability tests were carried out using half cells. The cells were charged and discharged at the same C-rates ranging from 0.2 C to 20 C. 1 C = 170 mA g⁻¹ was used in this work.

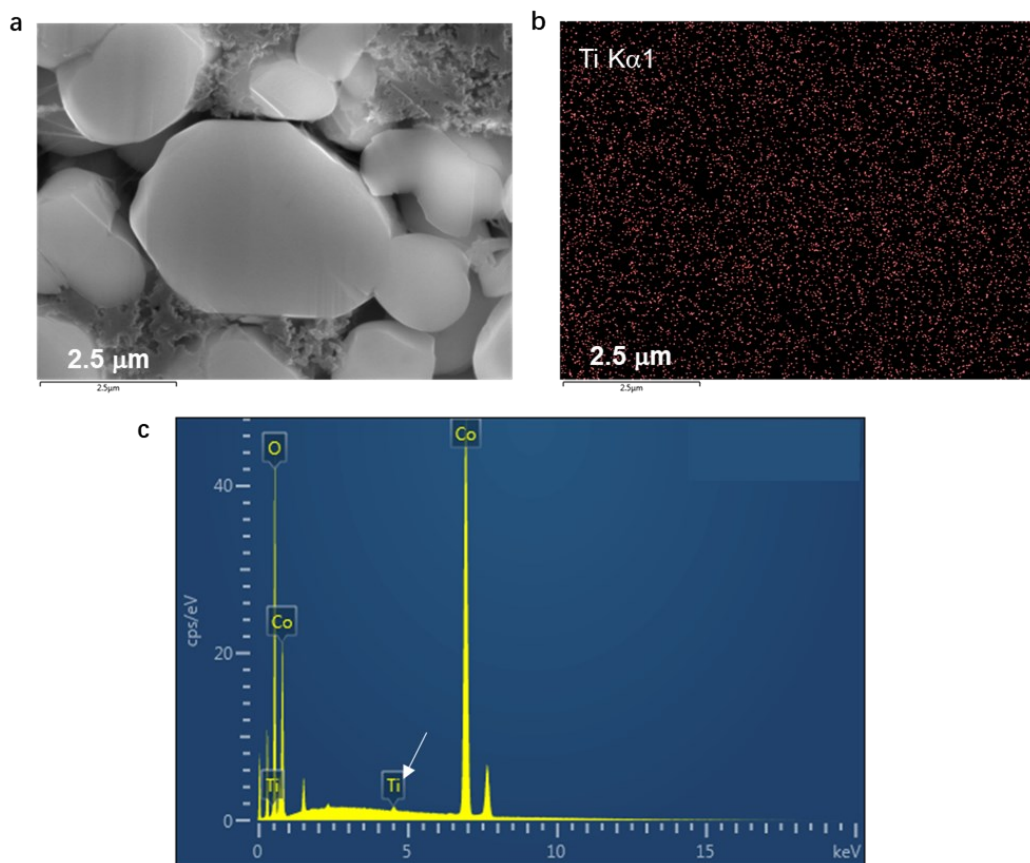
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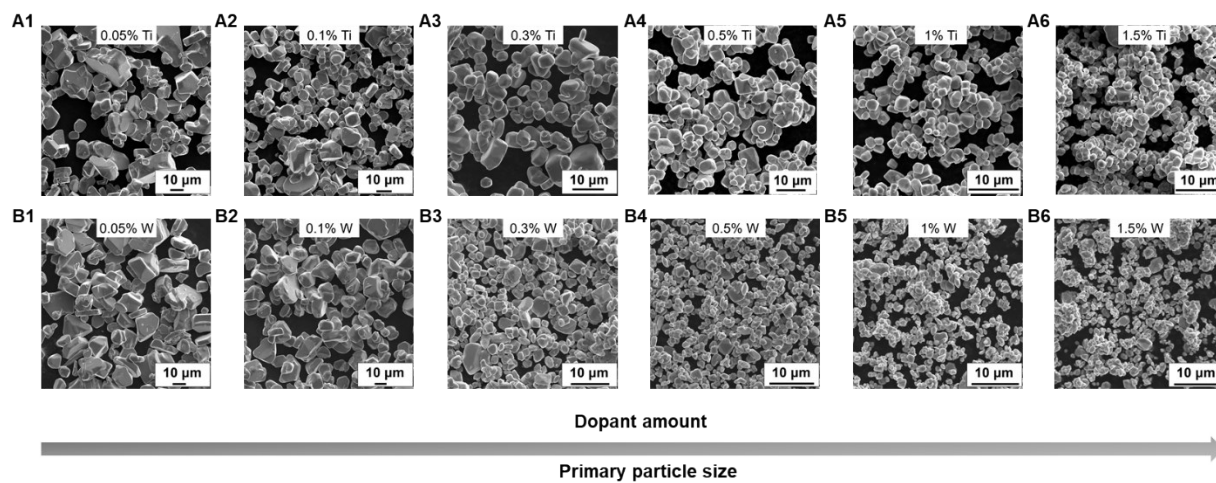
Supplementary Figures



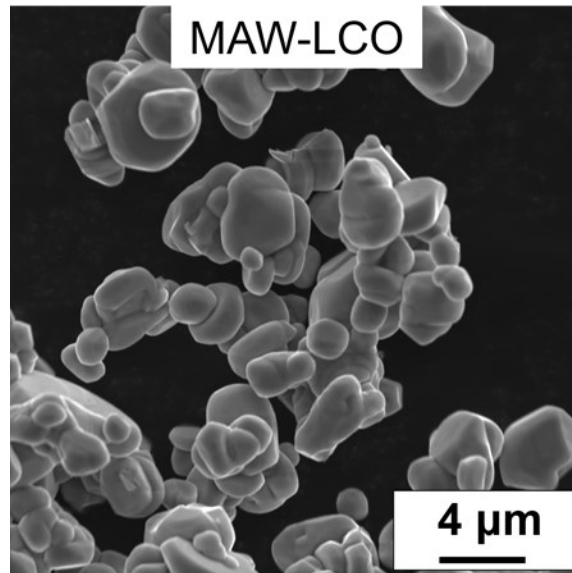
Supplementary Fig. 1 | Powered X-ray diffraction patterns for the bare and doped LCO samples. All the patterns could be indexed as hexagonal LiCoO_2 .



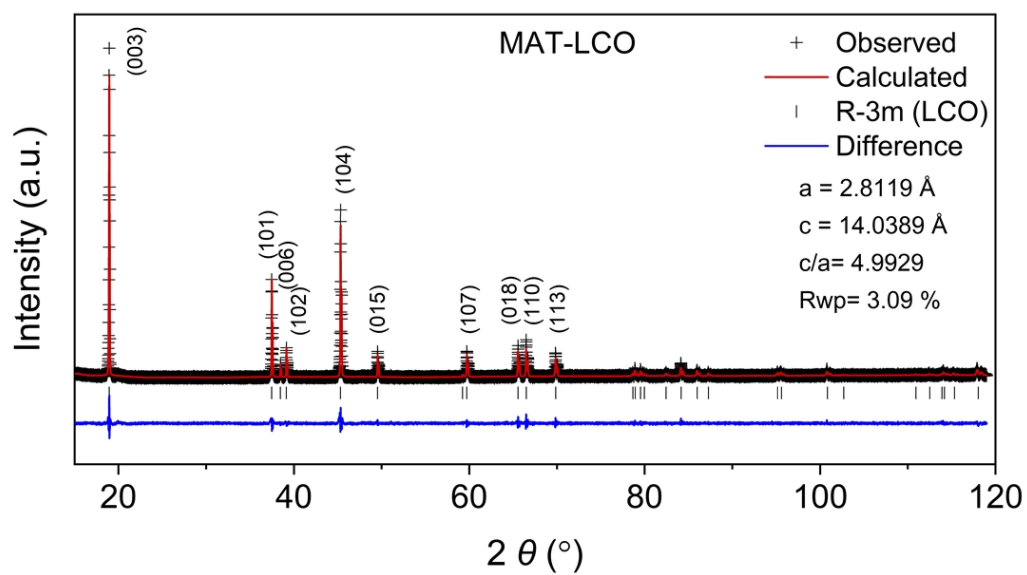
Supplementary Fig. 2 | (a) Cross-sectional SEM image of the Ti-doped LiCoO₂ sample. The cross section was prepared using ion-milling. (b) and (c) are EDX mapping result of Ti and the corresponding spectrum from this particular region, respectively.



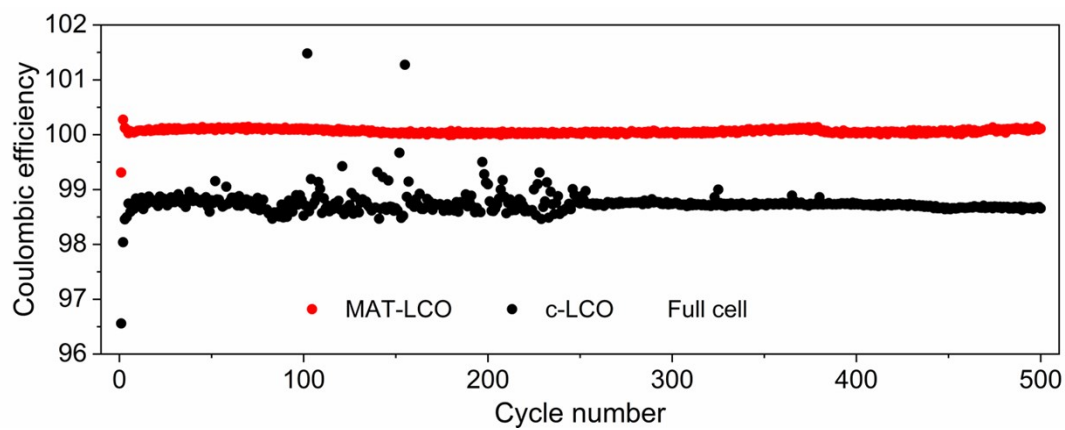
Supplementary Fig. 3 | SEM micrographs of LCO particles synthesized with Ti or W as the dopant. (A1 to A6) and (B1 to B6) show the gradual reduction of the LCO primary particle size as a function of the dopant concentration for Ti and W (relative to Co mol%), respectively. TiO_2 and WO_3 were used.



Supplementary Fig. 4 | SEM micrograph of LCO particles synthesized with Mg, Al, and W as co-dopants. W^{6+} ions were also used as the crystal growth mediator. 0.1 wt% of $Mg(OH)_2$, $Al(OH)_3$, and WO_3 were added to the molten salt synthesis of $LiCoO_2$ in $LiOH-Li_2SO_4$.



Supplementary Fig. 5 | Powder X-ray diffraction of the MAT-LCO and the rietveld refinement results.



Supplementary Fig. 6 | Comparison of the coulombic efficiencies of the LCO-graphite full cells cycled in the voltage range of 4.4–2.9 V.

Supplementary Table 1**Surface energies for (0001) and (10 $\bar{1}$ 4) LCO surfaces with different dopants (in $J m^{-2}$)**

Dopants	Co	Al	Mg	Mo	Ti	W	Nb	Zr
(0001) surface	2.181	2.219	1.950	1.910	1.900	1.168	1.63	1.884
(10 $\bar{1}$ 4) surface	1.111	1.064	1.037	0.953	0.966	0.906	0.978	0.945