

12-17-2014

## A Reversible and Stable Flake-Like LiCoO<sub>2</sub> Cathode for Lithium Ion Batteries

Tao Wei

Rui Zeng

Yongming Sun

Yunhui Huang

Kevin Huang

University of South Carolina - Columbia, huang46@cec.sc.edu

Follow this and additional works at: [https://scholarcommons.sc.edu/emec\\_facpub](https://scholarcommons.sc.edu/emec_facpub)

 Part of the [Mechanical Engineering Commons](#)

---

### Publication Info

Published in *Chemical Communications*, Volume 50, Issue 16, 2014, pages 1962-1964.

©Chemical Communications (2014), Royal Society of Chemistry.

This article cannot be redistributed or further made available.

This article was first published by the Royal Society of Chemistry and can be found at <http://dx.doi.org/10.1039/C3CC48559E>

Wei, T., Zeng, R., Sun, Y., Huang, Y., & Huang, K. (2014). A Reversible and Stable Flake-Like LiCoO<sub>2</sub> Cathode for Lithium Ion Batteries. *Chemical Communications*, 50 (16), 1962-1964. <http://dx.doi.org/10.1039/C3CC48559E>

This Article is brought to you by the Mechanical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact [digres@mailbox.sc.edu](mailto:digres@mailbox.sc.edu).

# A reversible and stable flake-like LiCoO<sub>2</sub> cathode for lithium ion batteries†

 Cite this: *Chem. Commun.*, 2014, 50, 1962

 Tao Wei,<sup>ab</sup> Rui Zeng,<sup>b</sup> Yongming Sun,<sup>b</sup> Yunhui Huang<sup>\*b</sup> and Kevin Huang<sup>\*a</sup>

 Received 8th November 2013,  
 Accepted 16th December 2013

DOI: 10.1039/c3cc48559e

[www.rsc.org/chemcomm](http://www.rsc.org/chemcomm)

**A dense and thick flake-like cathode structure was demonstrated to have a preferential crystallographic orientation for Li<sup>+</sup> migration and a better tolerance to cracking, both of which enable a reversible and stable capacity at moderate rates from 0.1 to 2 C.**

With a widespread commercial use of lithium ion battery (LIB) technology in portable consumer electronic devices such as laptops and cellular phones, there is growing interest in applying this technology to all-electric/hybrid vehicles and grid energy storage. While new battery chemistries such as Li-S,<sup>1</sup> Li-air,<sup>2</sup> and Na-ion batteries<sup>3</sup> are currently being investigated as the alternatives to overcome the barriers, continuous optimization in the properties of existing materials for commercial LIB in an effort to improve the reversible capacity and safety, on the other hand, has received constant interest.

The state-of-the-art LIBs use lithium salt in an organic solvent as the electrolyte, graphite as the anode and the material of choice among LiCoO<sub>2</sub>, LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub> or Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> as the cathode. Layer structured LiCoO<sub>2</sub> is still considered the most important commercial cathode for LIB owing to its high voltage, high reversible capacity and long cycle stability, despite its high price and slight toxicity.

The improvement of commercial LIBs has been mainly focused on retaining capacity, stability and safety at the highest rates possible. Rate capability is one of the key properties for LIBs to be employed in large power consumption applications such as all-electric/hybrid vehicles and grid energy storage.<sup>4</sup> Mounting experimental evidence has suggested that decreasing the particle size by nanostructuring LiCoO<sub>2</sub> can render high charge-discharge rates as a result of increased electrode-electrolyte contact area and a shortened migration pathway for Li<sup>+</sup> transport.<sup>5</sup> On the other

hand, controlling the morphology is another way to enhance the rate performance, one example of which is the “balls” structured LiCoO<sub>2</sub> prepared by the so-called “desert rose” method.<sup>6</sup>

For practical applications, safety is the most important issue to consider. Although the nanoscaled cathode materials have been demonstrated to provide excellent capacity at high rates,<sup>4b,7</sup> they also present a serious safety problem. The chemical interactions between electrolyte and electrodes can lead to the formation of a solid electrolyte interphase (SEI) and overheating; the latter, if not properly controlled, can ignite the organic solvent and cause fire.<sup>4a,8</sup> So far, operating an LIB at rates from 0.1 to 2 C can satisfy most of the needs for ordinary cellular phones and laptops. To fabricate 0.1–2 C LIBs without invoking safety problems, cathode materials with particle size in micrometers are necessary. In fact, micro-sized LiCoO<sub>2</sub> is the most used cathode material for commercial LIBs.

Other noted work on improving the capacity, stability and safety of the commercial LiCoO<sub>2</sub> cathode is to coat it with oxides such as La<sub>2</sub>O<sub>3</sub>,<sup>9</sup> TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> and others.<sup>10</sup> The major advantage of surface coating is the prevention of Co<sup>4+</sup> formed during high-voltage charging from dissolving into the liquid electrolyte and further destabilizing the layered structure, causing capacity fade.

When considering improving the cycle stability of the LiCoO<sub>2</sub> cathode, the stress/strain induced by electrochemical charge (Li<sup>+</sup> de-intercalation) and discharge (Li<sup>+</sup> intercalation) must be minimized.<sup>10b,11</sup> If not, the shearing stress can cause a non-uniform dimensional change within the particle, and consequently result in fractures and decrease in the conductivity. One solution is to modify the surface with a metal oxide such as ZrO<sub>2</sub> to achieve a zero-strain state, which has been shown to greatly improve the cycle life of the LiCoO<sub>2</sub> cathode.<sup>10b</sup>

In this work, we demonstrate improved capacity and cycle stability at 0.1–2 C by controlling the morphology of LiCoO<sub>2</sub> cathode particles. Xiao *et al.* previously showed that the nanoscaled flake-like LiCoO<sub>2</sub> possesses an excellent initial capacity,<sup>7b</sup> but the cycle performance faded quickly upon cycling. The inability of nano-plate LiCoO<sub>2</sub> cathodes to resist the internal strain by the non-uniform dimensional change and the propensity to react with the liquid electrolyte are believed to be the main reasons for the

<sup>a</sup> Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA. E-mail: kevin.huang@sc.edu

<sup>b</sup> 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

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc48559e

capacity fade. In this study, we show synthesis of micro-sized LiCoO<sub>2</sub> with thick and dense flake morphology (termed “flake-like LiCoO<sub>2</sub>”). Such a dense and thick flake structure is expected to be stronger than the nano-sized flake structure to resist damage caused by internal strain/stress. The flake-like LiCoO<sub>2</sub> has a smaller specific area surface to contact with the liquid electrolyte, yielding less reaction and Co<sup>4+</sup> dissolution. These attributes ensure micro-sized flake-like LiCoO<sub>2</sub> to exhibit excellent reversible capacity, long-term cycle stability and safety with reasonable capacity retained. According to a study in ref. 12, the similar micro-sized flake-like LiMn<sub>0.4</sub>Ni<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub> (LMNC) cathode indeed exhibits a higher capacity and longer cycle life than those with nanostructured ones.

The micro-sized flake-like LiCoO<sub>2</sub> cathode was synthesized by a two-step method described in the ESI† as well as in our previous work.<sup>13</sup> CoO nanoplates were used as the precursors to produce LiCoO<sub>2</sub>. Their scanning electron microscope (SEM) images are shown in Fig. 1a. The CoO nano-plates exhibit a dimension of 2–4 μm in width and 10 nm in thickness. The LiCoO<sub>2</sub> flakes were formed by reacting CoO nano-plates with LiOH·H<sub>2</sub>O, followed by calcination at 850 °C in air for 10 h. The surface area analyzed by the BET method is 0.8 m<sup>2</sup> g<sup>-1</sup>. The phase of LiCoO<sub>2</sub> was confirmed by XRD, as presented in Table 1, to possess a *c/a* = 4.993, indicating a layered structure. The morphology of the micro-sized LiCoO<sub>2</sub> particles shown in Fig. 1b clearly shows a thick (~0.85 μm) and dense flake morphology. As indicated by the selected area electron diffraction (SAED) pattern along the [001] zone axis direction shown in Fig. 1c and Fig. S6 and S8 of the ESI,† the flake-like LiCoO<sub>2</sub> possesses preferentially exposed non-electrochemical active (001) planes and electrochemically active planes (100) and (010) on the straight edges for Li<sup>+</sup> diffusion.

It is common to observe a large degree of cation disorder in the layered α-NaFeO<sub>2</sub> structured cathode materials. When transition metal (such as cobalt) atoms are misplaced on the Li<sup>+</sup> sites, the Li<sup>+</sup> pathways would be disrupted along with increased attraction between the neighboring MO<sub>2</sub> sheets, thus lowering the Li<sup>+</sup> mobility and capacity.<sup>14</sup> For the flake-like

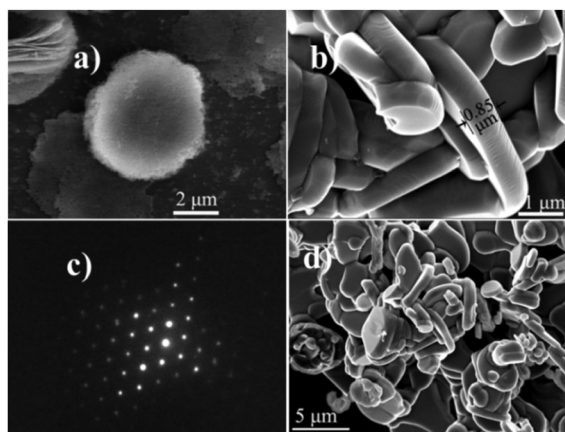
**Table 1** Room-temperature lattice parameters, Co atom occupancy, and *c/a* value obtained by Rietveld refinement of XRD patterns obtained from original flake-like LiCoO<sub>2</sub> powder, tested LiCoO<sub>2</sub> and Li<sub>0.33</sub>CoO<sub>2</sub> powders for 100 cycles

	Original powder	Tested LiCoO <sub>2</sub>	Tested Li <sub>0.33</sub> CoO <sub>2</sub>
<i>a</i> (Å)	2.8153	2.8104	2.8087
<i>c</i> (Å)	14.0573	14.0579	14.3104
<i>V</i> (Å <sup>3</sup> )	97.2065	97.3195	98.3361
Co(1) <sub>occupancy</sub>	0.98(4)	0.97(6)	0.98(7)
<i>R</i> <sub>wp</sub>	6.38%	5.47%	8.97%
<i>c/a</i>	4.993	5.002	5.095

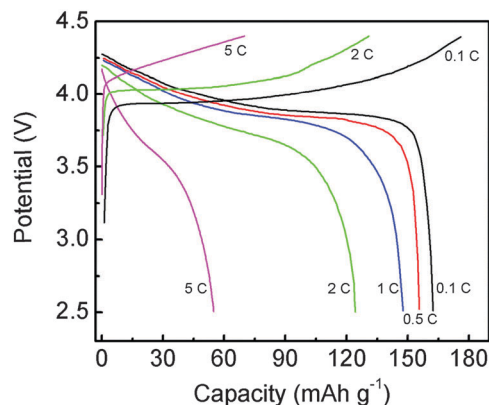
LiCoO<sub>2</sub>, however, only 2% Li<sup>+</sup>/Co<sup>3+</sup> disorder was found by Rietveld refinement as shown in Table 1. High sintering temperature and long sintering time are believed to have promoted cation diffusion, and then minimized the misplacement of Co atoms on the Li<sup>+</sup> sites.

Charge–discharge characteristics of coin-type cells with the micro-sized flake-like LiCoO<sub>2</sub> cathode are shown in Fig. 2. The galvanostatic discharge capacity is 163 mA h g<sup>-1</sup>. At 1 C, the charge and discharge capacities are 159 (not shown in Fig. 2) and 148 mA h g<sup>-1</sup>, respectively, whereas at 2 C, the charge and discharge capacities decrease to 131 and 123 mA h g<sup>-1</sup>, respectively. Compared with the 4.2 V cut-off voltage commonly used for LIBs, the higher 4.4 V cut-off voltage used for this cathode enables a higher discharge capacity. Some independent groups have also confirmed that the micro-sized LiCoO<sub>2</sub> sintered at high temperatures for longer time yields better capacity in the very first few cycles.<sup>5a,10a,15</sup>

At 5 C, however, the flake-like LiCoO<sub>2</sub> cathode showed a drastic reduction in capacity even after the first cycle. This finding is consistent with Shi's study,<sup>12</sup> where the similar micro-sized flake-like LNMC exhibits good reversible capacity at 0.1, 0.5, 1 and even 2 C, but not at 5 C. For the similar flake like but nano-sized LiCoO<sub>2</sub> cathode, this was not the case; even at 5 C it showed a rather high capacity.<sup>7b</sup> We believe that the high surface area possessed by the nano-sized LiCoO<sub>2</sub> was the main factor which maintained the high rate, even though it was not sustainable for an extended period due to its high reactivity with the electrolyte.



**Fig. 1** (a) FESEM images of the as-synthesized CoO nanoparticles; (b) the dense and thick flake-like LiCoO<sub>2</sub>; (c) the SAED pattern of flake-like LiCoO<sub>2</sub>; (d) FESEM images of the tested flake LiCoO<sub>2</sub> for 100 cycles.



**Fig. 2** Voltage versus capacity profiles for flake-like LiCoO<sub>2</sub> at rates of 0.1, 0.5, 1, 2 and 5 C. The cells were cycled in the voltage range of 2.5–4.4 V at 25 °C.

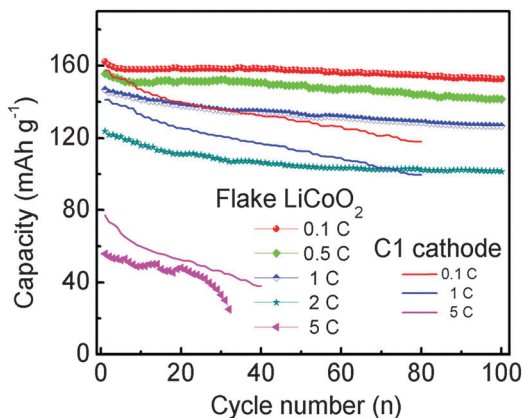


Fig. 3 Galvanostatic discharge capacities vs. cycle number; voltage window: 2.5–4.4 V; rate: 0.1, 0.5, 1, 2 and 5 C for flake-like LiCoO<sub>2</sub> and C1 cathode.

For comparison, we also synthesized a normal LiCoO<sub>2</sub> cathode (named C1) by a solid state reaction. Fig. 3 shows the galvanostatic discharge profiles for the flake-like LiCoO<sub>2</sub> and the C1 electrode cycled over the voltage range of 4.4–2.5 V vs. Li/Li<sup>+</sup>. It is evident that the flake-like LiCoO<sub>2</sub> has a higher initial discharge capacity, reversible capacity and cycle stability than C1 in the range from 0.1 to 2 C. The discharge capacity generally shows a gradual decrease for the initial few cycles, and then stabilizes for the rest of the cycles. The discharge capacity remains 153 mA h g<sup>-1</sup> at 0.1 C even after 100 charge–discharge cycles; this represents >93.9% retention in capacity. At 2 C, there is still about 81% capacity retained after 100 cycles, where the C1 cathode suffered a more pronounced capacity-decay. At 5 C, the flake-like morphology disappeared. Again, the unique morphology and low surface area are the main reasons for the difference observed between the flake-like and irregularly shaped LiCoO<sub>2</sub> cathodes.

To understand the failure mechanisms, the battery with the flake-like LiCoO<sub>2</sub> cathode was disassembled after 3 and 100 cycles, and the cathode powder was measured and examined by XRD, SEM and TEM. Table 1 presents crystallographic features of the original powders and those after 100 cycles, indicating a rather flat and high degree of Co<sup>3+</sup> ordering. The high degree of ordering is beneficial to avoid disturbing the Li<sup>+</sup> migration. It is also clear that the cycling actions on the LiCoO<sub>2</sub> cathode have caused a decrease in the *a* lattice and increase in the *c* lattice. For the Li<sub>0.33</sub>CoO<sub>2</sub> sample with 0.67 Li<sup>+</sup> removed by charging, a large volume increase between the two adjacent CoO<sub>2</sub> layers is observed. The micro-cracks shown in Fig. S9 (ESI<sup>†</sup>) for the sample after 3 cycles may explain why there was a capacity fading during the initial few cycles. Similar microstructures shown in Fig. S7 and S10 (ESI<sup>†</sup>) for the samples after 100 cycles seem to suggest that the micro-cracks induced during cycling occur only in the first few cycles. Once created, these micro-cracks remain relatively unchanged

for the rest of the cycles with stability. Moreover, this micron-sized dense and thick flake structure takes up less space when compared with nano or macroporous structures. The tap-density of this powder is as high as 2.78 g cm<sup>-3</sup>, which is suitable for achieving high volumetric energy density.

In summary, the dense and thick flake-like structure cathode was demonstrated to have a preferential crystallographic orientation for Li<sup>+</sup> migration and a better tolerance to cracking, both of which enable a reversible and stable capacity at moderate rates from 0.1 to 2 C. Should safety and capacity retention be considered the first priority, the low surface-area flake-like LiCoO<sub>2</sub> presented in this study would be a better choice for LIBs.

Y. H. H. is grateful for support from the National Natural Science Foundation of China (No. 51361130151).

## Notes and references

- (a) P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J.-M. Tarascon, *Nat. Mater.*, 2012, **11**, 19; (b) W. Weng, V. G. Pol and K. Amine, *Adv. Mater.*, 2013, **25**, 1608.
- (a) Z. Peng, S. A. Freunberger, Y. Chen and P. G. Bruce, *Science*, 2012, **337**, 563–566; (b) H.-D. Lim, K.-Y. Park, H. Song, E. Y. Jang, H. Gwon, J. Kim, Y. H. Kim, M. D. Lima, R. O. Robles, X. Lepró, R. H. Baughman and K. Kang, *Adv. Mater.*, 2013, **25**, 1348.
- (a) M. D. Slater, D. Kim, E. Lee and C. S. Johnson, *Adv. Funct. Mater.*, 2013, **23**, 947; (b) N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada and S. Komaba, *Nat. Mater.*, 2012, **11**, 512.
- (a) J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359; (b) M. Okubo, E. Hosono, J. Kim, M. Enomoto, N. Kojima, T. Kudo, H. Zhou and I. Honma, *J. Am. Chem. Soc.*, 2007, **129**, 7444.
- (a) Y.-G. Guo, J.-S. Hu and L.-J. Wan, *Adv. Mater.*, 2008, **20**, 2878; (b) A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon and W. van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366; (c) P. G. Bruce, B. Scrosati and J.-M. Tarascon, *Angew. Chem., Int. Ed.*, 2008, **47**, 2930.
- (a) H. Chen, L. Wu, L. Zhang, Y. Zhu and C. P. Grey, *J. Am. Chem. Soc.*, 2010, **133**, 262; (b) H. Chen and C. P. Grey, *Adv. Mater.*, 2008, **20**, 2206.
- (a) D. Wang, X. Ma, Y. Wang, L. Wang, Z. Wang, W. Zheng, X. He, J. Li, Q. Peng and Y. Li, *Nano Res.*, 2010, **3**, 1; (b) X. Xiao, X. Liu, L. Wang, H. Zhao, Z. Hu, X. He and Y. Li, *Nano Res.*, 2012, **5**, 395.
- J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee and B. Park, *Angew. Chem., Int. Ed.*, 2003, **42**, 1618.
- P. Ghosh, S. Mahanty and R. N. Basu, *Electrochim. Acta*, 2009, **54**, 1654.
- (a) H.-M. Cheng, F.-M. Wang, J. P. Chu, R. Santhanam, J. Rick and S.-C. Lo, *J. Phys. Chem. C*, 2012, **116**, 7629; (b) J. Cho, Y. J. Kim, T.-J. Kim and B. Park, *Angew. Chem., Int. Ed.*, 2001, **40**, 3367.
- (a) Y. I. Jang, B. Huang, H. Wang, D. R. Sadoway, G. Ceder, Y. M. Chiang, H. Liu and H. Tamura, *J. Electrochem. Soc.*, 1999, **146**, 862; (b) H. Wang, Y. I. Jang, B. Huang, D. R. Sadoway and Y. M. Chiang, *J. Electrochem. Soc.*, 1999, **146**, 473–480; (c) M. Y. Song, D. S. Lee and D. R. Mumm, *Mater. Res. Bull.*, 2006, **41**, 1720–1728.
- S. J. Shi, Y. J. Mai, Y. Y. Tang, C. D. Gu, X. L. Wang and J. P. Tu, *Electrochim. Acta*, 2012, **77**, 39.
- Y. Sun, X. Hu, W. Luo and Y. Huang, *J. Mater. Chem.*, 2012, **22**, 13826.
- S. B. Schougaard, J. Bréger, M. Jiang, C. P. Grey and J. B. Goodenough, *Adv. Mater.*, 2006, **18**, 905.
- (a) R. Sathiyamoorthi, R. Chandrasekaran, A. Gopalan and T. Vasudevan, *Mater. Res. Bull.*, 2008, **43**, 1401; (b) J. Ying, C. Jiang and C. Wan, *J. Power Sources*, 2004, **129**, 264; (c) M. Jo, Y.-S. Hong, J. Choo and J. Cho, *J. Electrochem. Soc.*, 2009, **156**, A430.