

Enhanced rate performance and cycling stability of CoCO_3 -polypyrrole composites for lithium ion battery anodes

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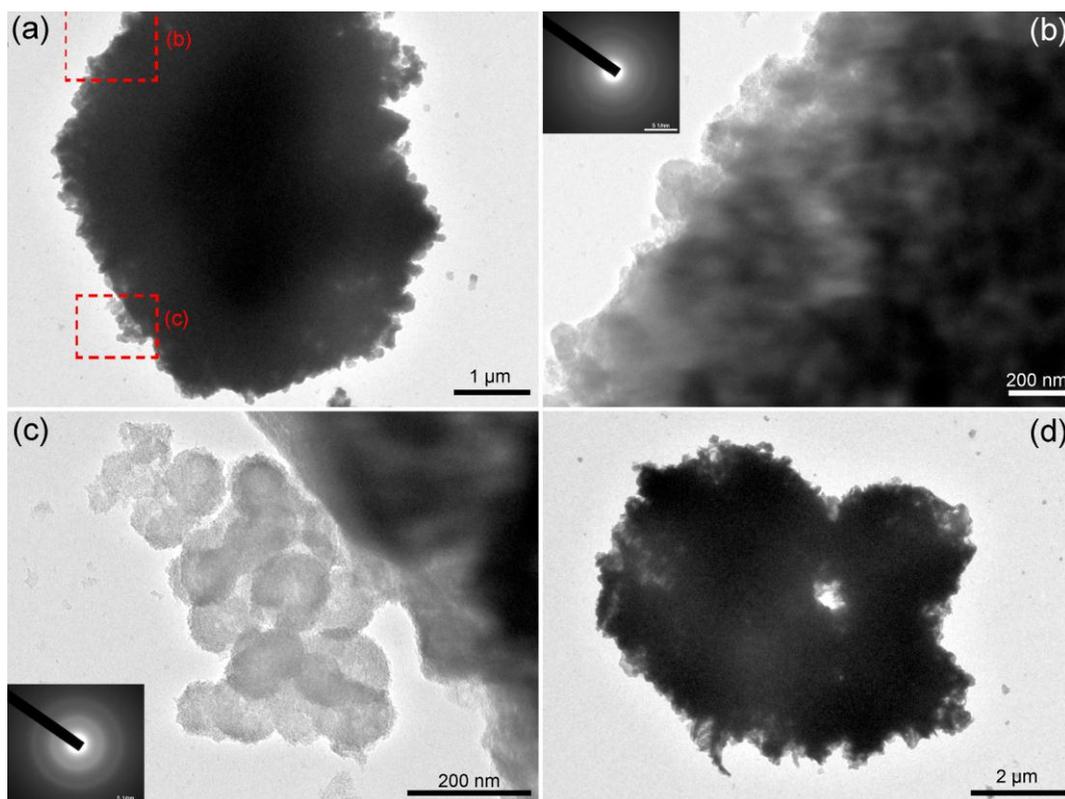


Fig. S1 (a and d) TEM images of CC-PPy. (b and c) Partial enlarged TEM images of (a), inset with the corresponding SAED patterns.

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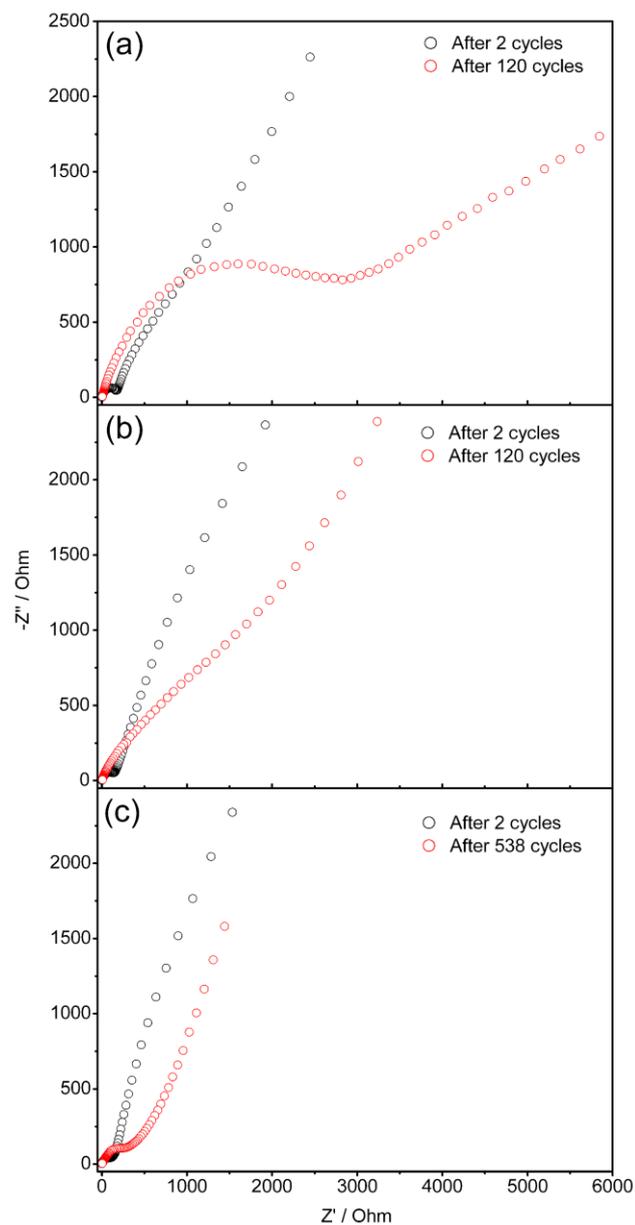


Fig. S2 Nyquist plots of (a) CC and (b) CC-PPy electrodes after 2 and 120 cycles. (c) Nyquist plot of CC-PPy electrode after 2 and 538 cycles.

To understand the kinetic factors for better cycling performance of CC-PPy, Fig. S2 presents the Nyquist plots of the two electrodes after 2 and 120 cycles from 0.1 to 2 C, as well as that of CC-PPy electrode after 2 and 538 cycles from 0.1C to 5C. The corresponding cycling performance was shown in Fig. 4b and c of the body text. All the plots share the common feature of a depressed semicircle followed by a low-frequency line. The intersection between the semicircle and the x axis is an indication to the overall impedance comprising the surface film and the charge-transfer resistance R_t ($R_{SEI}+R_{ct}$).¹⁻² And the low-frequency line represents the Warburg impedance (Z_w), which is related to solid-state lithium diffusion in the electrode. A steeper line generally indicates higher lithium ion conductivity.³⁻⁴ As shown in Fig. Sa and b, CC-PPy electrode exhibits smaller R_t and Z_w after two cycles at 0.1 C. The superiority becomes more obvious after 120 cycles, where CC shows significantly increased R_t and decreased low-frequency slope while CC-PPy shows smaller R_t and slightly decreased slope. The increased non-uniformity of the electrode caused by volume swing and particle aggregation during cycling is the main reason for the severely declined charge-transfer and lithium diffusion ability of CC. PPy layer not only improve the conductivity of the electrode, but also compensate for the volume change and prevent the detachment and agglomeration of pulverized $CoCO_3$, thus resulting in more facile electrode kinetics of CC-PPy.

Surprisingly, R_t of CC-PPy electrode increased marginally after 538 cycles at various rates from 0.1 to 5 C (Fig. S2c), being much lower than the value after 120 cycles. The low-frequency slope also changed a little. This agrees well with its great recovery capability shown in Fig 4c and the possible reasons are analyzed as follows.

Although the overall shape of the starting particles of CC-PPy could be preserved by PPy layer, the inner nanorods still tend to disintegrate with volume swing until a stable SEI film formed on their surface. Comparing the crystal structure of $CoCO_3$, Li_2CO_3 and Li_2O , the volume variation of 'second-order' reaction is probably larger than that of 'first-order' one. However, not all cycles shown in Fig 4b and c involved 'second-order' reaction. Here we suppose 'second-order' reaction likely occurs in one cycle only if it delivers a charge capacity beyond 700 mA h g^{-1} , considering the theoretical value of 'first-order' reaction of CC-PPy ($\sim 415.3\text{ mA h g}^{-1}$) and the extra reversible capacity caused by capacitive lithium storage ($\sim 200\text{ mA h g}^{-1}$). As shown in Fig. 4c, there are only 8 cycles meeting this condition in the initial 50 cycles, whereas all the initial 50 cycles of CC-PPy in Fig. 4b deliver a capacity of more than 780 mA h g^{-1} . A stable SEI film is considered to be formed after 50 cycles and the electrode integrity then suffers from slight damage in the following cycling. Therefore, due to much less 'second-order' reactions thus smaller volume variation in the initial 50 cycles of Fig. 4c than Fig 4b, CC-PPy keeps better electrode uniformity thus shows smaller R_t value and larger Warburg slope after 538 cycles than after 120 cycles. The results indicate that multiple high-rate cycles, which can more effectively keep electrode integrity, is a suitable activation method for modified $CoCO_3$ anode.

References

- [1] Q. Q. Xiong, J. P. Tu, Y. Lu, J. Chen, Y. X. Yu, Y. Q. Qiao, X. L. Wang and C. D. Gu, *J. Phys. Chem. C*, 2012, **116**, 6495.
- [2] E. Kang, Y. S. Jung, G. H. Kim, J. Chun, U. Wiesner, A. C. Dillon, J. K. Kim and J. Lee, *Adv. Funct. Mater.*, 2011, 21, 4349.
- [3] Y. Ma, C. Zhang, G. Ji and J. Y. Lee, *J. Mater. Chem.*, 2012, 22, 7845.
- [4] J. Y. Xiang, J. P. Tu, Y. Q. Qiao, X. L. Wang, J. Zhong, D. Zhang and C. D. Gu, *J. Phys. Chem. C*, 2011, 115, 2505.