Supporting Information

Reversible Reduction of Li₂CO₃
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1 XRD patterns and Raman of Li₂C₂
Li₂C₂ was received from Prof. Xiaoyan Song in Beijing University of Technology. They reported the preparation of Li₂C₂ in Ref. [1]). Its XRD and Raman patterns were shown in Figure S1. The major phase of the material is Li₂C₂ though some impurity peaks (asterisks marked) can be observed (Figure S1a). The impurity phase is metallic lithium (PDF card No. 01-1264). Amorphous carbon, as precursor for Li₂C₂, might exist in the sample, but cannot be recognized by XRD. The central position in Raman peak for symmetrical stretching vibration of C≡C appears at 1873 cm⁻¹ (Figure S1b).

![Figure S1. XRD and Raman pattern of the as-prepared Li₂C₂](image)

2 FTIR
Although the FTIR spectra of commercial CoCO₃ and Li₂CO₃ are very similar to each other, their difference is as clear (Figure S2). The weak peak at ca. 500 cm⁻¹ in Li₂CO₃ (for Li-O vibration) becomes indistinguishable in CoCO₃ (the Co-O vibration is supposed to be below 500 cm⁻¹ because Co is heavier than Li and the Co-O bond is weaker than the Li-O bond). In addition, the strong and double peak of Li₂CO₃ at 1490 and 1430 cm⁻¹ (vibration for C=O in CO₃²⁻) becomes a broad plateau centered at 1466 cm⁻¹ in CoCO₃. Therefore, it is easy to distinguish the presence or absence of CoCO₃ and Li₂CO₃ by FTIR spectroscopy. The FTIR spectra of Li₂C₂ (the same as for the XRD test) and Li₂O are also shown in Figure S2. It is clear that both of them have strong absorptions below 1000 cm⁻¹. They are vibration for Li-C and Li-O.

![Figure S2. FTIR spectra of the Li₂CO₃, CoCO₃, Li₂C₂ and Li₂O](image)
3 FFT images of the HRTEM in the article

![FFT images](image)

**Figure S3** Corresponding FFT of the HRTEM images for Figure 4 in the main article

4 HRTEM

More HRTEM images of CoCO₃ electrode at various discharge/charge states and the corresponding FFT of the images are shown in Figure S4. It is clear that the crystallinity of the CoCO₃ is high (Figure S4a). When the CoCO₃/Li cell is discharged to 0.7 V vs. Li⁺/Li, domains of Li₂CO₃ and metallic Co grains are clearly seen (Figure S4b). This means that CoCO₃ is decomposed to Li₂CO₃ and metallic Co at 0.7 V. When the cell is finally recharged to 3.0 V, vague fringes can be recognized in very small areas (Figure S4c and d), implying the low crystallinity of the regenerated CoCO₃. By Fourier transformation treatment, dotted rings appear (inset of Figure S4c and d. A simple calculation indicates that all these rings correspond to CoCO₃ as are indexed in the images.
Figure S4. HRTEM images of the CoCO$_3$ electrode at various discharge/charge states and the corresponding FFT of the images (insets): the prepare CoCO$_3$ (a), discharged to 0.7 V (b), recharged to 3.0 V (c and d)

References