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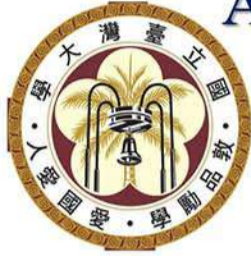
境外生研究獎學金

Research Scholarship for International Graduate Students

Revealing the Absence of Carbon in Aprotic Li-CO₂ Batteries: A Mechanism Study Toward CO₂ Reduction under a Pure CO₂ Environment

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Abstract

While attention is focused on Li-CO₂ batteries due to their high energy density and ability to utilize carbon, their detailed cathodic reaction mechanism remains unclear. Thus far, the recognized reaction formula involves CO₂ reduction with carbon as the reduced product ($3\text{CO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$, $E^\circ = 2.8 \text{ V vs. Li}^+/\text{Li}$). However, evidence of carbon formation is seldom provided in previous studies. The potential of the potential-determining step ($\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^-$, $E^\circ = 1.1 \text{ V vs. Li}^+/\text{Li}$) in the reaction is much lower than the common working potential (2.6 V). Furthermore, the calculated redox potential at 2.8 V itself is incorrect since the calculation includes chemical reaction(s) that does not involve electron transfer. These findings do not suggest that the proposed cell reaction is correct. Herein, we propose that the previously observed reaction is caused by O₂ and H₂O participating in the electrochemical reaction to give such a high working potential. The formation of Li₂CO₃ as the only discharge product can support our statement through the examination of soft X-ray absorption spectroscopy. Moreover, we find the reaction of sole CO₂ reduction can only happen at a low potential of 1.1 V with a current density of 100 mA g⁻¹. CO, rather than C, is found to be the discharge product. Thus, both O₂ and H₂O contamination should be considered when studying Li-CO₂ batteries, and the discharge product should be characterized carefully to claim the reaction formula.

Results

Part I Revealing the absence of carbon

Electrochemical tests & XRD

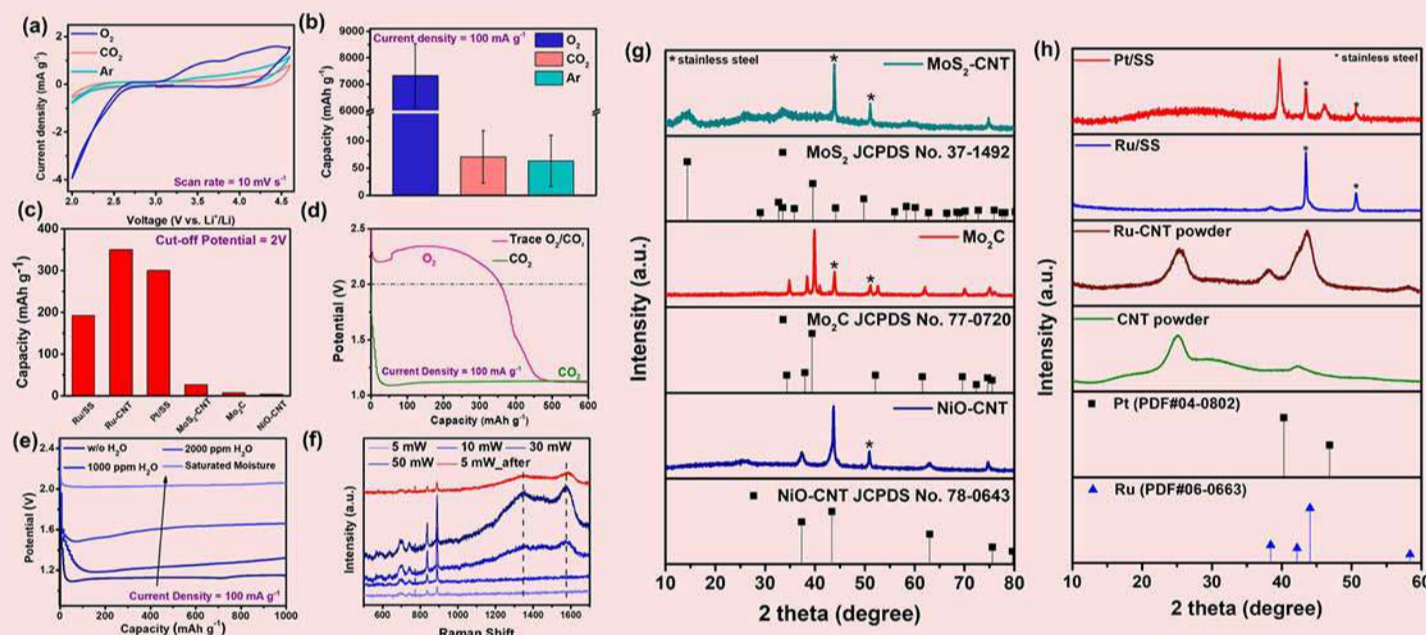


Figure 1. (a) Cyclic voltammetry (CV) tests and (b) statistics on the full-discharge capacity of Li-CO₂ batteries under three different gas atmospheres using CNTs cathodes. (c) Full-discharge capacities of Li-CO₂ batteries with different catalysts. (d) Galvanostatic discharge test of Li-CO₂ battery with (pink curve) and without (green curve) trace oxygen. (e) Galvanostatic discharge tests of Li-CO₂ batteries using CNTs/SS under different contents of water. (f) Raman spectra of a gold cathode measured under different laser power in a Li-CO₂ battery. (g)(h) XRD patterns of applied catalysts.

SEM

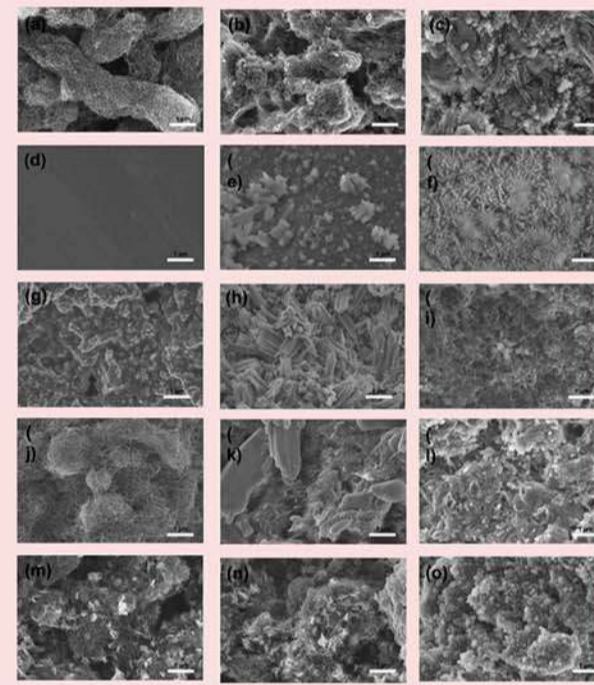


Figure 2. SEM images of (a) pristine CNTs, (b) 2V-CNTs, (c) 1V-CNTs, (d) pristine Pt, (e) 2V-Pt, (f) 1V-Pt, (g) pristine MoS₂/CNT, (h) 2V-MoS₂/CNT, (i) 1V-MoS₂/CNT, (j) pristine Mo₂C, (k) 2V-Mo₂C, (l) 1V-Mo₂C, (m) pristine NiO/CNT, (n) 2V-NiO/CNT, and (o) 1V-NiO/CNT electrodes.

Soft X-ray absorption spectroscopy (SXAS)

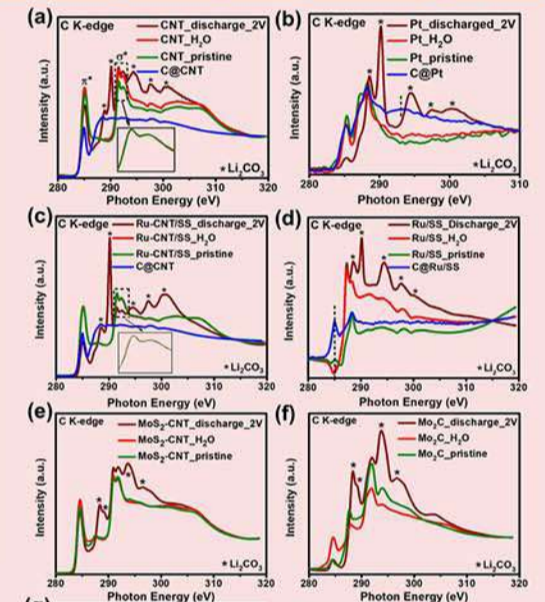


Figure 3. SXAS spectra of (a) CNTs, (b) Pt, (c) Ru/SS, (d) Ru/SS, (e) MoS₂-CNT, (f) Mo₂C, and (g) NiO-CNT cathodes under different treatments. The inset of (a) and (c) shows the magnification of the framed region.

Part II Determination of the true discharge products

Electrochemical tests

SXAS & Raman

In situ tests & Proposed mechanism

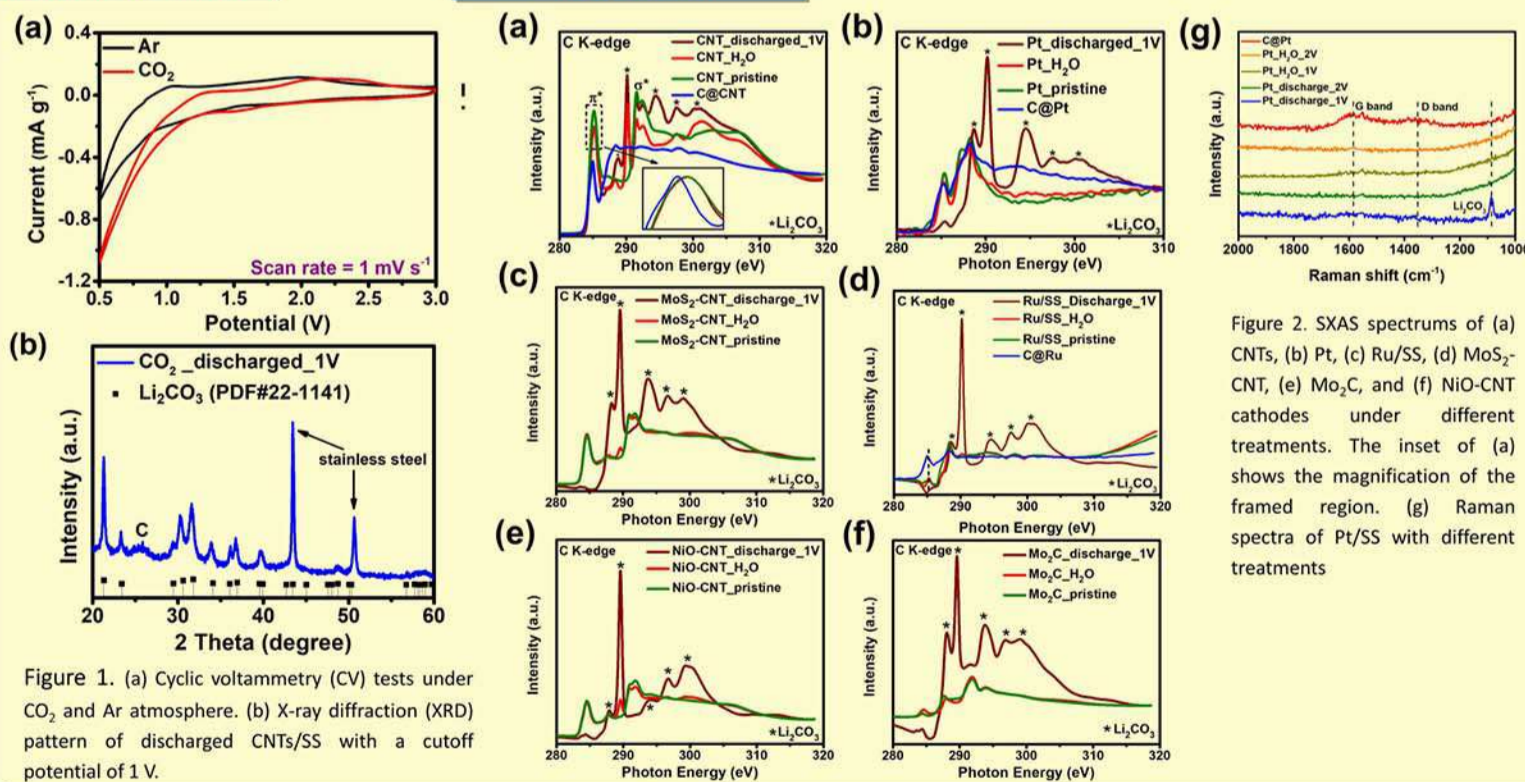


Figure 1. (a) Cyclic voltammetry (CV) tests under CO₂ and Ar atmosphere. (b) X-ray diffraction (XRD) pattern of discharged CNTs/SS with a cutoff potential of 1 V.

Figure 2. SXAS spectra of (a) CNTs, (b) Pt, (c) Ru/SS, (d) MoS₂-CNT, (e) Mo₂C, and (f) NiO-CNT cathodes under different treatments. The inset of (a) shows the magnification of the framed region. (g) Raman spectra of Pt/SS with different treatments.

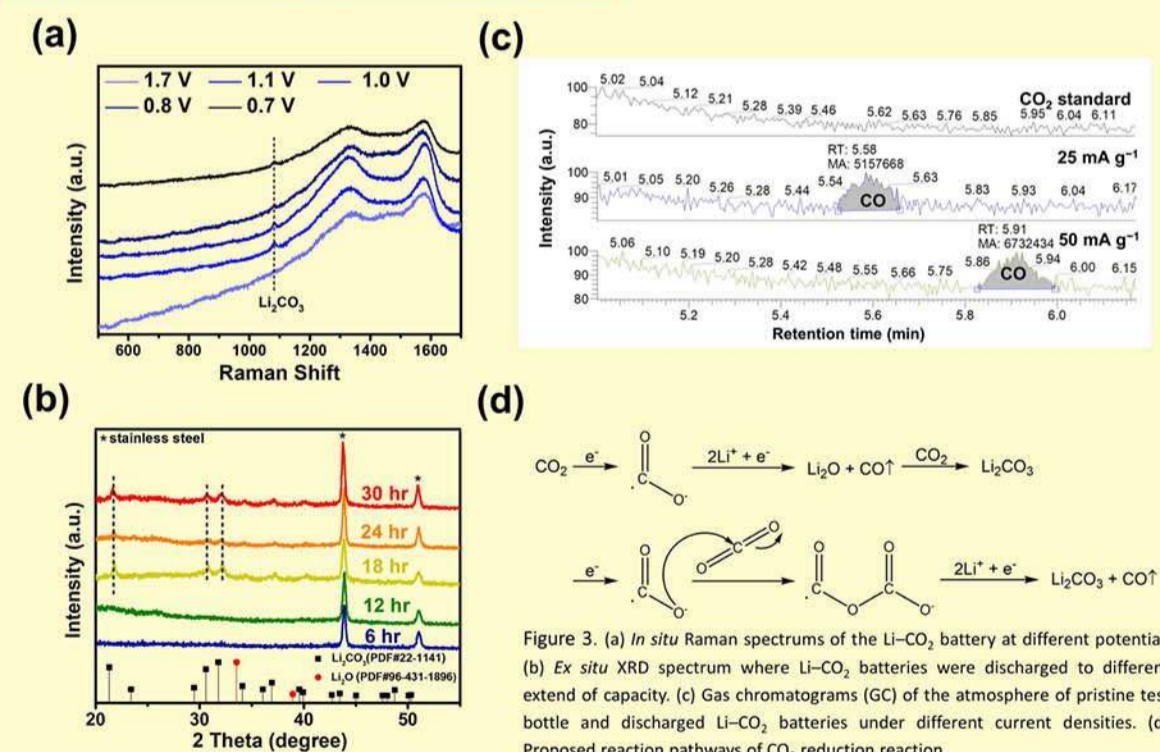


Figure 3. (a) In situ Raman spectra of the Li-CO₂ battery at different potential. (b) Ex situ XRD spectrum where Li-CO₂ batteries were discharged to different extend of capacity. (c) Gas chromatograms (GC) of the atmosphere of pristine test bottle and discharged Li-CO₂ batteries under different current densities. (d) Proposed reaction pathways of CO₂ reduction reaction.

Conclusions

In summary, we discover that carbon was not formed during the discharge process. Instead, CO is formed at low potential of < 2 V. The reaction above 2 V should be mainly contributed by O₂ and/or H₂O contaminants. We propose that the widely recognized reaction that forms carbon is not correct. To achieve a sustainable Li-CO₂ battery, H₂O-assisted strategy may be a solution to reduce the large overpotential of CO₂ reduction and evolution reactions in aprotic solvent.

Acknowledgements

The authors would like to thank the Ministry of Science and Technology of Taiwan (Contract Nos. NSTC 107-2113-M-002-008-MY3, NSTC 109-2113-M-002-020-MY3, NSTC 110-3116-F-011-002, NSTC 109-2112-M-003-011, and NSTC 110-2112-M-003-016) for financially supporting this research.

Publication

Iputera, K.; Huang, J.Y.; Haw, S.C.; Chen, J.M.; Hu, S.F.; Liu, R.S., Revealing the Absence of Carbon in Aprotic Li-CO₂ Batteries: A Mechanism Study toward CO₂ Reduction under a Pure CO₂ Environment. J. Mater. Chem. A 2022, 10, 3460–3468.



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