

# Utilizing CO<sub>2</sub> in an Energy Storage System

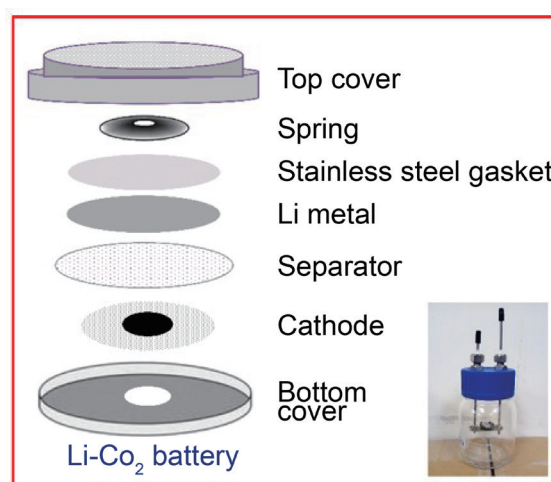
*Li-CO<sub>2</sub> batteries with high energy efficiency are key to CO<sub>2</sub> utilization. Sluggish kinetics limit their practical application, but electrocatalysts may be a solution to this.*

The development of portable devices has led to the pursuit of high-energy-density storage systems. To date, Li-ion batteries (LIB) have predominantly been used in energy storage systems as they provide considerable energy density with a high energy efficiency of approximately 90%. To replace LIBs, it has been proposed that the graphite anode could be replaced with Li metal. It is notable that Li metal can provide a capacity that is 10 times larger than that of the graphite anode, thus boosting the battery's overall energy density. On the cathode side, CO<sub>2</sub> has been proposed to be a suitable candidate as its redox potential (2.8 V vs. Li/Li<sup>+</sup>) is comparable to that of the LiFePO<sub>4</sub> cathode (3.4 V vs. Li/Li<sup>+</sup>), with the former also weighing less than the LiFePO<sub>4</sub> cathode.

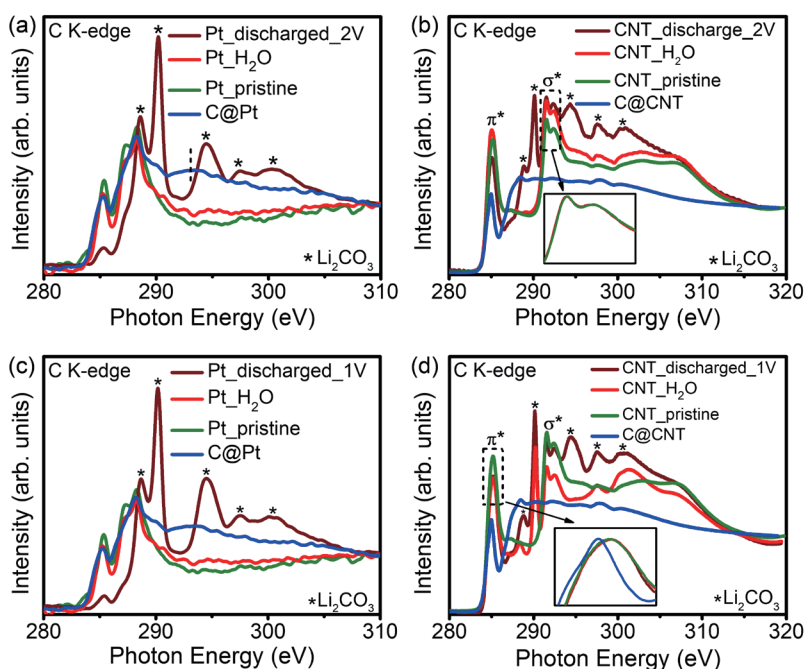
When a cell discharges, CO<sub>2</sub> is reduced to C according to the following cell equation:  $4\text{Li} + 3\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$ . Moreover, the use of CO<sub>2</sub> in the battery system indicates the possibility of CO<sub>2</sub> utilization. Combining these two novel electrodes, a Li-CO<sub>2</sub> battery with an energy density of 1876 Wh/kg can be developed. **Figure 1** shows a typical Li-CO<sub>2</sub> battery in which coin cells with holes that permit CO<sub>2</sub> flow are sealed into a glass bottle filled with CO<sub>2</sub> for electrochemical tests. However, Li-CO<sub>2</sub> batteries faces problems such as a high discharge/charge overpotential due to their sluggish kinetics. The discharge product, Li<sub>2</sub>CO<sub>3</sub>, is an electric and ionic insulator, which results in a high charge overpotential. When discharging, the intrinsically stable CO<sub>2</sub> must be reduced. In the commonly applied aprotic environment, CO<sub>2</sub> can hardly be reduced, which results in a high discharge overpotential. As a result, an effective electrocatalyst is required to not only reduce the overpotential but also increase the energy efficiency.

The teams of Ru-Shi Liu (National Taiwan University) and Jin-Ming Chen (NSRRC) recently studied the reaction mechanism of Li-CO<sub>2</sub> batteries using soft X-ray absorption spectroscopy (sXAS) at **TLS 20A1.1**. Considerable information can be obtained as changes in the reactants can be probed using C K-edge XAS. The team found that the major discharge product is Li<sub>2</sub>CO<sub>3</sub> with no C signals observed. This observation held irrespective of

whether the cells were discharged to 2 V or 1 V, indicating that C was not formed throughout the discharge process, which was contrary to most reports on Li-CO<sub>2</sub> batteries. The team claimed that the reaction should instead be  $2\text{Li} + 2\text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{CO}$ , where CO could be detected



**Fig. 1:** Configuration of a typical Li-CO<sub>2</sub> battery. [Reproduced from Ref. 1]



**Fig. 2:** Soft X-ray spectra of (a,c) Pt and (b,d) carbon nanotube cathodes at different discharge states with different treatments. The H<sub>2</sub>O-washed discharged cathodes (red lines) resemble their pristine (brown lines) counterparts, indicating the absence of C. [Reproduced from Ref. 1]

using GC-MS. The discrepancy with previous reports could be attributed to the trace amounts of O<sub>2</sub> and/or H<sub>2</sub>O that participated in the reduction reaction. O<sub>2</sub> and H<sub>2</sub>O themselves could be reduced at approximately 3 V vs. Li/Li<sup>+</sup> and could act as electrocatalysts to promote CO<sub>2</sub> reduction. Combining the theoretical calculations and experimental results, they proposed that pure CO<sub>2</sub> could not be reduced to C at potentials above 2 V.

In summary, a suitable electrocatalyst is required to improve the discharge overpotential. Efforts should be devoted to the development of electrocatalysts that ease the charge-transfer reactions. From this point of view, O<sub>2</sub> and H<sub>2</sub>O could be good candidates as electrocatalysts, owing to their capability to increase the partial positive charge on C in CO<sub>2</sub>. However, as Li metal is highly reactive to both O<sub>2</sub> and H<sub>2</sub>O, electrocatalysts with good stability with respect

to the highly reductive Li should be developed. sXAS plays an important role in revealing the chemical states of the reactants in Li-CO<sub>2</sub> batteries. In the future, an *in situ* sXAS setup would further benefit the mechanism study. (Reported by Kevin Iputera, National Taiwan University)

*This report features the work of Ru-Shi Liu and his collaborators published in J. Mater. Chem. A* **10**, 3460 (2022).

### TLS 20A1 XAS

- sXAS
- CO<sub>2</sub> Reduction, Li-CO<sub>2</sub> Battery, Electrocatalyst, Chemistry

### Reference

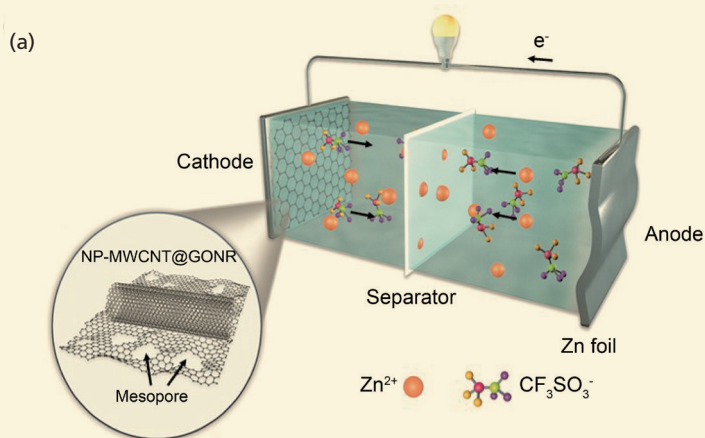
1. K. Iputera, J. Y. Huang, S. C. Haw, J. M. Chen, S. F. Hu, R. S. Liu, *J. Mater. Chem. A* **10**, 3460 (2022).

## Adding a Protective Layer for Aqueous Zinc Ion Capacitors

*A mechanism study of zinc dendrite suppression used in situ transmission X-ray microscopy.*

Aqueous zinc-ion capacitors (ZIC) have recently attracted attention as promising energy-storage devices for portable electronics and large-scale energy-storage systems, owing to their low cost, high stability, high safety, high power, and high energy density.<sup>1</sup> A ZIC comprises a battery-type Zn metal anode (prepared by Zn plating and stripping) and a supercapacitor-type cathode (that provides a high double-layer capacitance or pseudocapacitance), as illustrated in **Fig. 1(a)**. Supercapacitor-type cathode materials are usually high-surface-area carbons, e.g., activated carbon,<sup>3</sup> graphene,<sup>4</sup> carbon nanotubes,<sup>5</sup> and mesoporous carbon.<sup>6</sup> Graphene exhibits a double-layer capacitance among these carbon materials, owing to its high theoretical surface area (2630 m<sup>2</sup> g<sup>-1</sup>) and high electrical conductivity.<sup>7</sup> In addition, carbon materials with porous structures exhibit a high surface area and porosity, which can facilitate ion diffusion and the accumulation of a considerable number of charges, enhancing the double-layer capacitance.<sup>8</sup> A Zn foil anode is promising for mass production because of its low cost and high theoretical capacity (820 mAh g<sup>-1</sup>).<sup>1</sup> However, the main challenge concerns the formation of Zn dendrite on the anode, which results in short circuits and capacity decay. Different approaches have been employed to suppress the dendrite formation on the anode, such as using a three-dimensional Zn structure, ion distributors, and artificial solid electrolyte interphase as protection layers.<sup>9</sup>

Wei-Hsiang Lin, Han-Yi Chen (National Tsing Hua University), Chia-Liang Sun (Chang Gung University), Ming-Hsien Lin (National Defense University), Chun-Chieh Wang (NSRRC), and their research teams have proposed the use of a high-surface-area nanoporous core-shell-structured multiwalled carbon nanotube@graphene oxide nanoribbon (NP-MWCNT@GONR), which is prepared by using a facile microwave-assisted method as illustrated in **Fig. 1(b)**, as the cathode material and protection layer in aqueous ZICs.<sup>10</sup> The MWCNTs in the core-shell structure inhibit the restacking of the graphene layers, which can significantly enhance the cycling stability. In addition, MWCNTs possess high electronic conductivity, which



**Fig. 1:** (a) Schematic of the NP-MWCNT@GONR//Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>/Zn.