using GC-MS. The discrepancy with previous reports could be attributed to the trace amounts of O_2 and/or H_2O that participated in the reduction reaction. O_2 and H_2O themselves could be reduced at approximately 3 V vs. Li/Li$^+$ and could act as electrocatalysts to promote CO_2 reduction. Combining the theoretical calculations and experimental results, they proposed that pure CO_2 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_2 and H_2O could be good candidates as electrocatalysts, owing to their capability to increase the partial positive charge on C in CO_2. However, as Li metal is highly reactive to both O_2 and H_2O, 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_2 batteries. In the future, an *in situ* sXAS setup would further benefit the mechanism study. (Reported by Kevin Iputera, National Taiwan University)

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TLS 20A1 XAS
- sXAS
- CO_2 Reduction, Li-CO_2 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.[1] 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,[3] graphene,[4] carbon nanotubes,[5] and mesoporous carbon.[6] Graphene exhibits a double-layer capacitance among these carbon materials, owing to its high theoretical surface area (2630 m^2 g^{-1}) and high electrical conductivity.[7] 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.[8] A Zn foil anode is promising for mass production because of its low cost and high theoretical capacity (820 mAh g^{-1}).[1] 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.[9]

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.[10] 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
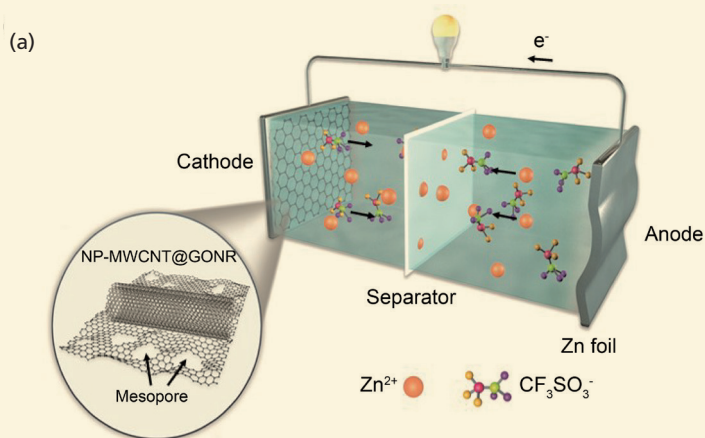

Fig. 1: (a) Schematic of the NP-MWCNT@GONR//Zn(CF$_3$SO$_3$)$_2$//Zn.

facilitates direct electron transfer, while GONRs with nanopores offer a high surface area to store a large number of ions, thus enhancing the double-layer capacitance. As a result, the NP-MWCNT@GONR exhibits a considerably higher capacity, rate performance, energy density, and power density as a cathode material in a Zn-ion liquid electrolyte than the MWCNT and MWCNT@GONR.

The NP-MWCNT@GONR in 3 M $Zn(CF_3SO_3)$ liquid electrolyte exhibited a high energy density of 90.09 Wh kg^{-1} at 95 W kg^{-1} and high power density of 19 kW kg^{-1} at 30.55 Wh kg^{-1}, with the capacity
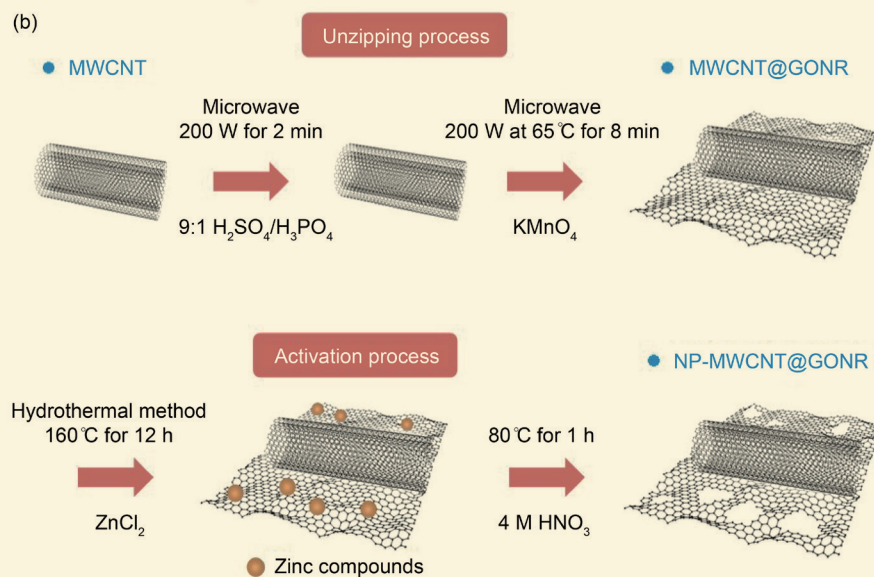

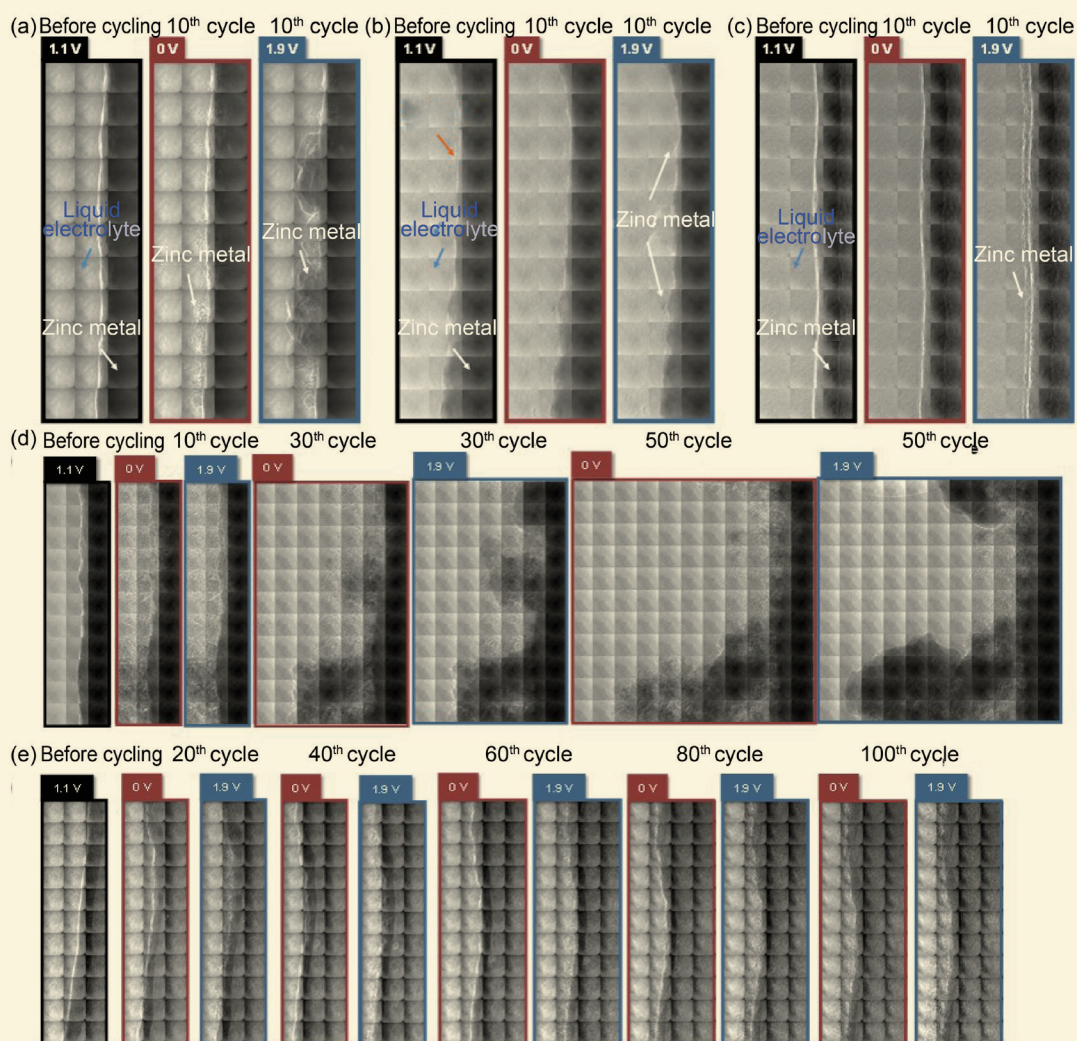**Fig. 1**: (b) Synthesis of the NP-MWCNT@GONR. [Reproduced from Ref. 10]

Fig. 2: *In situ* TXM images of the Zn foil anode at 5 A g^{-1} in (a) NP-MWCNT@GONR//Zn with a liquid electrolyte, (b) NP-MWCNT@GONR//Zn@NP-MWCNT@GONR with a liquid electrolyte, and (c) NP-MWCNT@GONR//Zn gel electrolyte before and after 10 cycles. *In situ* TXM images of dendrite growth on the Zn foil at 1 A g^{-1} in the (d) liquid and (e) gel electrolytes. [Reproduced from Ref. 10]

retention reaching 86.5% after 200 cycles. However, this ZIC with a liquid electrolyte suffered from Zn dendrite formation on the anode and deposition of Zn compounds on the cathode, leading to device failure after 200 cycles. Therefore, the NP-MWCNT@GONR was coated on the anode to inhibit Zn dendrite formation and improve the cycle stability up to 3,000 cycles. Furthermore, PVA-Zn(CF$_3$SO$_3$) gel electrolytes were used to suppress Zn dendrite formation on the anode and unexpected Zn compound deposition on the cathode because of their high viscosity and relatively slow ion diffusion. The cycle life of the ZIC with the gel electrolyte improved to 2,000 cycles, revealing excellent long-term stability. Furthermore, the devices with the gel electrolyte exhibited self-healing properties, which are useful for portable and wearable electronics.

The formation of Zn dendrite in liquid and gel electrolyte systems was observed using transmission X-ray microscopy (TXM) at the **TLS 01B1**. The *in situ* synchrotron TXM analyses (**Fig. 2**) show that the NP-MWCNT@GONR protective layer coating and freeze-dried gel electrolyte effectively inhibited dendrite growth on the anode and enhanced the reversibility of Zn compound deposition on the cathode, thus improving the long-term stability of the ZICs. **Figure 3** summarizes the morphological changes of the Zn foil anode during the Zn stripping and plating process.
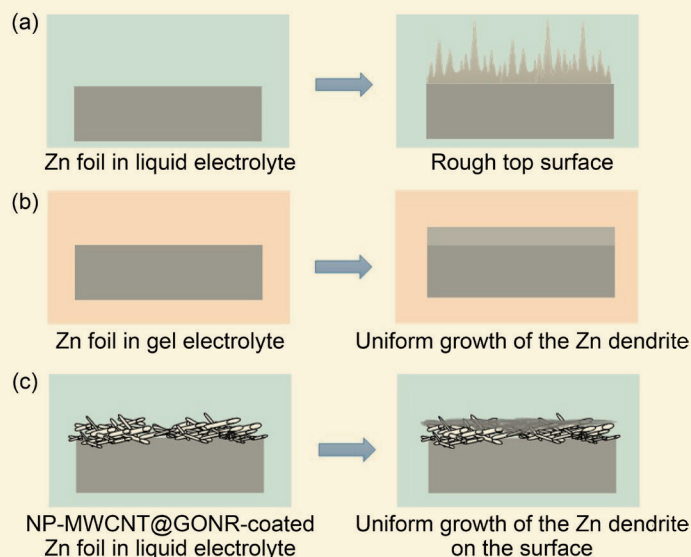

(a)

Zn foil in liquid electrolyte → Rough top surface

(b)

Zn foil in gel electrolyte → Uniform growth of the Zn dendrite

(c)

NP-MWCNT@GONR-coated Zn foil in liquid electrolyte → Uniform growth of the Zn dendrite on the surface

Fig. 3: Schematic illustrating the structural changes of the Zn foil anode during the Zn stripping and plating processes: (a) bare Zn foil in the liquid electrolyte, (b) bare Zn foil in the gel electrolyte, and (c) NP-MWCNT@GONR-coated Zn foil in the liquid electrolyte. [Reproduced from Ref. 10]

Moreover, the ZICs with freeze-dried gel electrolytes showed excellent bending and self-healing properties. In conclusion, this work successfully demonstrated that the NP-MWCNT@GONR could be a promising cathode and protection layer material for ZICs. In addition, the NP-MWCNT@GONR//PVA-Zn(CF$_3$SO$_3$)//Zn device achieved good capacity, excellent stability, high safety, and outstanding recoverability, which could be promising for the development of flexible and self-healable ZICs. (Reported by Han-Yi Chen, National Tsing Hua University)

*This report features the work of Han-Yi Chen and his collaborators published in J. Power Sources **541**, 231627 (2022).*

TLS 01B1 X-ray Microscopy
- TXM
- Materials Science, Chemistry, Surface, Interface Chemistry

References
1. M. Song, H. Tan, D. Chao, H. J. Fan, Adv. Funct. Mater. **28**, 1802564 (2018).
2. C. X. Xie, H. M. Zhang, W. B. Xu, W. Wang, X. F. Li, Angew. Chem. Int. Edit. **57**, 11171 (2018).
3. L. B. Dong, X. P. Ma, Y. Li, L. Zhao, W. B. Liu, J. Y. Cheng, C. J. Xu, B. H. Li, Q. H. Yang, F. Y. Kang, Energy Stor. Mater. **13**, 96 (2018).
4. S. L. Wu, Y. T. Chen, T. P. Jiao, J. Zhou, J. Y. Cheng, B. Liu, S. R. Yang, K. L. Zhang, W. J. Zhang, Adv. Energy Mater. **9**, 7 (2019).
5. S. L. Wang, Q. Wang, W. Zeng, M. Wang, L. M. Ruan, Y. A. Ma, Nanomicro Lett. **11**, 12 (2019).
6. C. H. Jiang, Z. M. Zou, Diam. Relat. Mat. **101**, 9 (2020).
7. G. G. Wallace, J. Chen, D. Li, S. E. Moulton, J. M. Razal, J. Mater. Chem. **20**, 3553 (2010).
8. G. Xiong, P. He, L. Liu, T. Chen, T. S. Fisher, Front. Energy Res. **3**, 39 (2015).
9. J. Yin, W. Zhang, N. A. Alhebshi, N. Salah, H. N. Alshareef, Adv. Energy Mater. **11**, 2100201 (2021).
10. W.-H. Lin, S.-F. Liu, S. Gull, T.-C. Su, K.-J. Tsai, C.-H. Kuo, C.-C. Lin, C.-C. Wang, M.-H. Lin, C.-L. Sun, H.-Y. Chen, J. Power Sources **541**, 231627 (2022).