

**Fig. 2:** Schematic illustration of photocatalytic conversion of  $\text{CH}_4$  to  $\text{C}_2\text{H}_4$  through surface alkoxy intermediates over a ZnO-AuPd hybrid. [Reproduced from Ref. 1]

In summary, the design of the atomically precise photocatalyst represents a prospective strategy to regulate the capability of catalyst dehydrogenation and to control the path of  $\text{CH}_4$  conversion. The ability to resolve fine

structures of atomically dispersed metal sites makes synchrotron-based XAFS spectroscopy an important technique to unravel the relations between catalyst structure and performance. (Reported by Chih-Wen Pao)

This report features the work of Yujie Xiong and his collaborators published in *J. Am. Chem. Soc.* **143**, 269 (2021).

#### TPS 44A Quick-scanning X-ray Absorption Spectroscopy

- XAS, Time-resolved XAS, XAFS,  $\mu\text{XFM}$
- Physics, Chemistry, Catalysis and Surface Science, Materials Science, Biology, Environmental Science

#### Reference

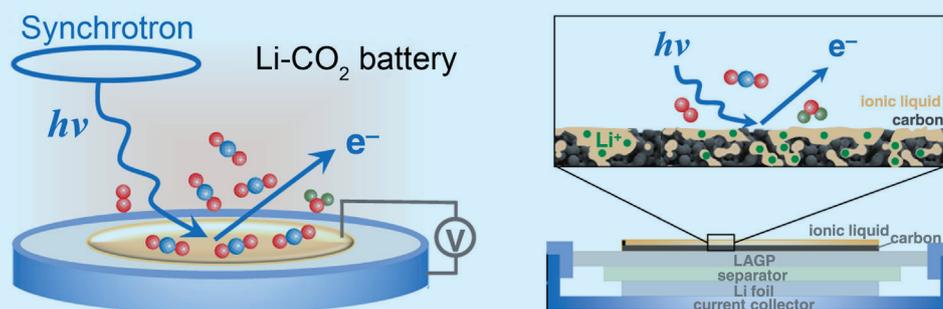
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## Unraveling the Cathode Chemistry of the Li-Battery Using Ambient-Pressure X-ray Photoelectron Spectra

Ambient-pressure X-ray photoelectron spectra showed that  $\text{H}_2\text{O}$  in a reaction mixture activated  $\text{Li-CO}_2$  in the battery discharge, producing unrecyclable carbonate. Conversely,  $\text{O}_2$  jumpstarted battery discharging while building recyclable amorphous carbon along with  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$ .

Rechargeable  $\text{Li-CO}_2$  batteries have attracted intense research attention for their potential as energy storage and  $\text{CO}_2$  fixation. Since the first demonstration of the prototypical design in 2013, cycle performance has been improved substantially, but further progress became sluggish due to a shortage of fundamental understanding. Several studies showed that  $\text{Li-CO}_2$  obtains a moderate capacity during discharging in pure  $\text{CO}_2$ . Based thereon, it was suggested that the cathode undergoes a  $\text{CO}_2$ -to-C transformation, denoted as a  $\text{CO}_2$  reduction reaction (CRR). Other studies showed, however, that the discharge capacity is negligible in pure  $\text{CO}_2$  and requires  $\text{O}_2$  at a particular proportion to accelerate the reaction. This discrepancy in the CRR kinetic and reaction mechanism remains elusive.

Yi-Chun Lu (Chinese University of Hong Kong, China) collaborated with Chia-Hsin Wang and Yaw-Wen Yang (NSRRC), to study  $\text{Li-CO}_2$  batteries using ambient-pressure X-ray photoelectron spectra (APXPS), a technique that has become a standard means for studies *in situ* over the past two decades. The APXPS system in the NSRRC is currently setup at the beamline **TLS 24A1** for user operation. Thanks to the turbo pumping to the experimental vacuum vessel, this technique operates at a baseline pressure less than  $10^{-7}$  mbar. This condition allows a well controlled operating environment to be created for the battery system. Taking advantage thereof, the authors studied the composition of the cathode surface during charging and discharging of an ionic-liquid-based  $\text{Li-CO}_2$  battery; its structure is illustrated in **Fig. 1**. Under 5 mbar of pure  $\text{CO}_2$ , the authors found that the discharge current consisted solely of a non-faradaic double-layer charging, a conclusion based on the evolution of the ionic liquid electrolyte XPS. In parallel, no sign of carbonate or other new species was observed in the C 1s spectra of all discharging potential, indicating that  $\text{Li-CRR}$  is electrochemically inactive in pure  $\text{CO}_2$ .



**Fig. 1:** Illustrated Li-CO<sub>2</sub> battery for the APXPS study *in situ* at TLS 24A1. The ionic liquid is composed of [Pyr14]<sup>+</sup> and [TFSI]<sup>-</sup>. [Reproduced from Ref. 1]

Water vapor accounts for the third most abundant substance in the atmosphere; its concentration fluctuates temporally and geographically. The authors hypothesized that varied water content might be the primary cause of the capacity discrepancy reported in the literature. To examine, they studied the XPS behavior of a Li-CO<sub>2</sub> battery under 5 mbar of 2:1 CO<sub>2</sub> and H<sub>2</sub>O. They found that, when discharging at 1.7–1.2 V<sub>Li</sub>, a substantial accumulation of amorphous carbon species was accompanied by the growth of LiOH. This result indicated that H<sub>2</sub>O helps to reduce CO<sub>2</sub> to amorphous carbon in the presence of Li<sup>+</sup>. Further discharge to 1.0 V<sub>Li</sub> generated carbonate species from CO<sub>2</sub> and LiOH. This observation agrees with the authors' hypothesis that water vapor plays a critical role in promoting CRR in non-aqueous electrolytes. On the charging side of the cycle, the authors found a significantly decreased amorphous carbon and a mild loss of carbonate, of which the withdrawal exposed the subsurface LiOH. When charged to 4.9 V<sub>Li</sub>, a substantial amount of Li<sub>2</sub>CO<sub>3</sub> and LiOH remained on the electrode. This condition, unfortunately, indicated a poor rechargeability of the battery.

The story became quite different with the presence of O<sub>2</sub>. In a 5-mbar 2:1 CO<sub>2</sub>-O<sub>2</sub> mixture, strongly solvated Li<sup>+</sup> in an ionic liquid bonded more weakly with O<sub>2</sub><sup>-</sup>, the activated oxygen intermediate species that consequently initiated CRR. As a result, the dominating discharging carbon product became amorphous carbon instead of carbonate. To bridge the pressure gap between this APXPS model study and a battery working condition at 1 bar, the authors scaled up the CO<sub>2</sub>-O<sub>2</sub> mixture to 1 bar for an X-ray diffraction (XRD) experiment *in situ*. Although XRD is blind to amorphous carbon, it revealed that Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O, also seen in the APXPS experiment, appeared in a potential range of no carbonate. The battery for the APXPS experiment resumed 90% of its capacity after a charge. This reversibility is attributed to the simultaneous decomposition of Li<sub>2</sub>O<sub>2</sub>, Li<sub>2</sub>O and amorphous carbon, in addition to the absence of side reactions. (reported by Bo-Hong Liu)

*This report features the work of Yi-Chun Lu and her co-workers published in Nano Energy* **83**, 105830 (2021).

### TLS 24A1 XPS, UPS, XAS, APXPS

- APXPS, XPS, NEXAFS, UPS
- Materials Science, Chemistry, Surface, Interface and Thin-film Chemistry, Condensed-matter Physics

### Reference

1. Y. Wang, W. Wang, J. Xie, C.-H. Wang, Y.-W. Yang, Y.-C. Lu, *Nano Energy* **83**, 105830 (2021).

