



## ToF-SIMS STUDY OF THE ELECTROCHEMICAL ISOTOPE EFFECTS FOR THE LITHIUM-ION BATTERIES

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ToF-SIMS is a powerful tool for the analysis of surface materials at micrometer scale. More importantly, isotopic information can be acquired within the mass spectra, which is not available in many other surface analysis tools based on electromagnetic wave. In this work, we developed a ToF-SIMS based research paradigm to study the electrochemical isotope effects in lithium ion batteries.

Aqueous electrolytes based on heavy water (D<sub>2</sub>O) and light water (H<sub>2</sub>O) were prepared to reveal the electrochemical isotope effects between the hydrogen isotopes. Compared with the H<sub>2</sub>O-based electrolyte, the D<sub>2</sub>O-based electrolyte showed a broader electrochemical window, longer cycle life and favorable rate performance of aqueous Li-ion batteries including LiCoO<sub>2</sub> and LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> as cathode materials. ToF-SIMS analysis demonstrated that using the D<sub>2</sub>O-based electrolyte, the cycled LiCoO<sub>2</sub> cathode showed a higher content of Li and a higher Li/Co ratio in the bulk of the cathode material which proves inhibited Li/H co-intercalation. These results support the high anodic stability against operation of high-voltage layered oxide cathode materials using D<sub>2</sub>O-based electrolyte. It was reasoned that protium (H) and deuterium (D) have magnified isotope effects in physicochemical properties due to the significantly different atomic masses, covalent hydrogen–oxygen bond and intermolecular hydrogen bond. 1

Silicon oxide-graphite (SiO<sub>x</sub>-G) composites are promising anode materials for building practical high-energy Li-ion batteries. Previous studies mostly focused on the cycling aging, but the calendar aging has not received sufficient attention. In this work, ToF-SIMS imaging was employed to explore the mechanism of the calendar aging chemistry at single particle level, of fully lithiated SiO<sub>x</sub>-G electrodes in half-cells both at ambient and high temperature (60°C). <sup>6</sup>Li labeling excluded the interference from cathode, and ToF-SIMS revealed the significant migration of <sup>6</sup>Li from the lithiated graphite to the vicinal SiO<sub>x</sub> particles at 60°C. We concluded that high-temperature storage notably accelerates the aging process. 2

A model study based on a Li–S battery was performed to reveal the variation between the electrochemical properties of the two S isotopes (<sup>34</sup>S and <sup>32</sup>S). The Li–<sup>34</sup>S cell showed improved cathode reaction kinetics at the solid–liquid interface and inhibited shuttle of polysulfides through the electrolyte so that it demonstrates better cycling performance than the Li–<sup>32</sup>S cell. Therefore, an electrochemical separation method for <sup>32</sup>S/<sup>34</sup>S isotope was proposed. ToF-SIMS analysis revealed a notably higher separation factor at the cycled Li–metal anode than the conventional separation methods such as chemical exchange or distillation. ICP-MS also provided solid evidences for high separation factor of <sup>32</sup>S/<sup>34</sup>S in the cycled electrolyte. 3

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### References

1. J. Chou, Y. Zhao, X.-T. Li, W.-P. Wang, S.-J. Tan, Y.-H. Wang, J. Zhang, Y.-X. Yin, F. Wang, S. Xin\* and Y.-G. Guo\*, *Angew. Chem. Int. Ed.*, 2022, 61, e202203137.
2. Y. Zhang, W.-P. Wang, Y. Zhao\*, X. Zhang, H. Guo, H. Gao, D.-X. Xu, Y.-M. Zhao, G. Li, J.-Y. Liang\*, S. Xin\* and Y.-G. Guo, *Adv. Funct. Mater.*, 2024, 34, 2310309.
3. X.-T. Li#, Y. Zhao#, Y.-H. Zhu, W.-P. Wang, Y. Zhang, F. Wang, Y.-G. Guo, S. Xin\* and C. Bai\*, *Proc. Natl. Acad. Sci. USA*, 2024, 121, e2316564121.