'Volcano-shaped' trend enables rational design of polysulfide catalysts in lithium–sulfur batteries

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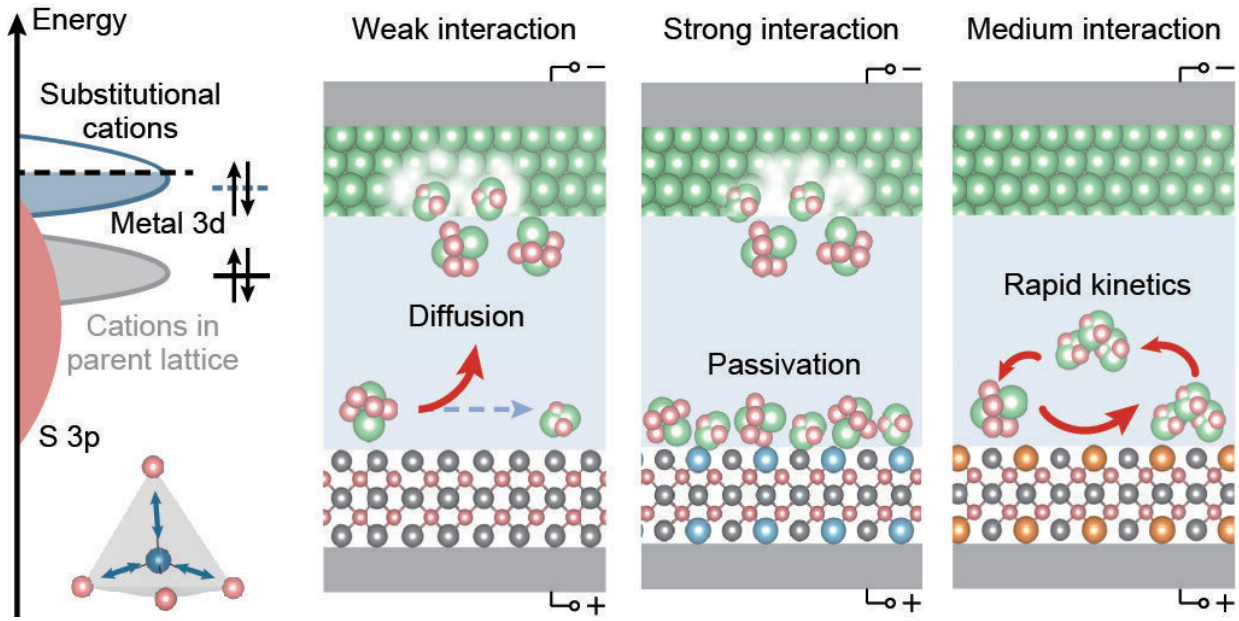

Schematic diagram of design principles for high-efficient lithium–sulfur catalysts. Credit: Shen Zihan

A joint research team led by Prof. Zhang Huigang from the Institute of Process Engineering (IPE) of the Chinese Academy of Sciences (CAS) and Dr. Lu Jun from Argonne National Laboratory, U.S.A., has found a "volcano-shaped" relationship between polysulfide adsorption and catalytic activity in lithium–sulfur (Li–S) batteries.

The study was published in *Nature Catalysis* on June 16.

According to Prof. Zhang, this volcano-shaped relationship may modify the long-standing principle that "strong adsorption of polysulfides leads to good catalytic activity."

The Li–S system shows great potential for next-generation batteries due to its high energy density. However, the sluggish kinetics of polysulfide conversion reactions leads to the "shuttling effect" and limits rate capability and cyclability, which hinder practical applications.

Recently, many experimental studies have reported that catalytic conversion of polysulfides plays a critical role in enhancing kinetics and suppressing polysulfide shuttling. Despite significant improvement in the electrochemical performance of Li–S batteries, studies on catalysts have heavily relied on trial and error and the governing principle has remained elusive.

In this study, the researchers demonstrated that, although a strong adsorption of polysulfides may lower the activation barrier for polysulfide conversion, it in turn impedes the desorption of products. This is due to the scaling principle since polysulfides (from Li_2S_8 to Li_2S_2/Li_2S) are sequentially adsorbed onto the same sites during charge/discharge.

To regulate the adsorption energy and maximize catalytic efficiency, they doped transition metal into the crystallographic framework of ZnS. The dopants were placed in stressed states and their d-orbitals were tuned accordingly. As a result, the adsorption energy had a linear relationship with the d-band center of dopants, but catalytic activity showed a "volcano-shaped" trend.

Such a discovery indicates that a long-standing assumption of

strengthening adsorption to enhance catalysis is invalid when desorption is rate limiting. "Catalysts and absorbents in a Li–S battery should be designed separately to improve the performance of Li–S batteries," said Prof. Zhang.

This study offers a rational basis for understanding the catalytic process of Li–S batteries at atomic or molecular levels and for designing new catalysts.

More information: Jun Lu, Cation-doped ZnS catalysts for polysulfide conversion in lithium–sulfur batteries, *Nature Catalysis* (2022). DOI: 10.1038/s41929-022-00804-4.
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