# Materials Science and Engineering Dissertation Defense

## Atomically Dispersed Electrocatalyst for Cathode Redox Reactions in Electrochemical Energy Storage

**School for Engineering of Matter, Transport and Energy**

**Xueyan Lin**
**Advisor: Zhaoyang Fan**

# Abstract

Conversion-type electrochemical energy storage offers high theoretical energy density but is frequently limited by sluggish multistep redox kinetics and unstable soluble intermediates. This dissertation develops a coherent design framework for atomically dispersed (single-atom and coordination-defined) electrocatalysts that accelerate conversion reactions by simultaneously engineering (i) the electronic structure of isolated metal centers and (ii) the ion/electron transport environment at the electrode level. The framework is demonstrated across lithium-sulfur (Li-S) and rechargeable zinc-air batteries.

First, a self-supporting, binder-free sulfur cathode is constructed by integrating Fe single-atom catalytic sites into a three-dimensional conductive aerogel. Fe-doped ZIF-derived N-doped carbon nanocages are anchored within a bacterial cellulose–derived carbon nanofiber network to form a freestanding scaffold that combines high conductivity, hierarchical porosity, and abundant exposed Fe-$N_x$ sites. Electrochemical and theoretical analyses reveal that the isolated Fe centers lower the energy barriers for S8 reduction to liquid polysulfides and further to solid Li2S2/Li2S, while promoting Li2S nucleation/deposition. The resulting site–framework synergy mitigates polysulfide shuttling and enables both high-rate and long-life operation (840 mAh g−1 at 2C and ~800 mAh g−1 after 500 cycles at 1C).

Second, in a collaboration work, a descriptor-guided strategy is established to rationally select transition-metal single-atom centers for sulfur redox. By combining density functional theory screening with a unified synthesis route, Ni-, Fe-, and Nb-doped graphitic hosts are prepared to validate predicted trends in Li-polysulfide/Li2S binding and conversion kinetics. Nb emerges as a standout center, delivering fast charge/discharge at 5C (679.3 mAh g−1) and durable cycling (837.5 mAh g−1 with 0.023% capacity decay per cycle after 500 cycles at 1C). Complementary Li2S dissolution tests and postmortem microscopy elucidate catalyst-dependent Li2S decomposition pathways, establishing a consistent theory-experiment design correlation.

Finally, the coordination-engineering principles are translated to oxygen electrocatalysis by introducing axial oxygen coordination at Nb single-atom sites to tune O-intermediate adsorption/desorption, achieving durable bifunctional ORR/OER activity. Implemented in rechargeable zinc-air batteries, the axially coordinated Nb sites enable >500 h continuous cycling at 10 mA cm−2 and a peak power density of 275 mW cm−2. Overall, this dissertation provides generalizable structure-function rules for atomically dispersed catalysts to overcome kinetic bottlenecks in conversion batteries.

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