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Cation Vacancies Regulate the Electron Spin Configuration of Cathode Catalytic Additives towards Robust Li-S Batteries

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Background

Lithium-sulfur batteries (LSBs) are promising energy storage devices due to their high theoretical energy density (2600 Wh kg-1), large specific capacity (1675 mAh g-1), potential cost-effectiveness, and environmental friendliness.[1] However, the commercialization of LSBs is limited by factors such as polysulfide migration, sluggish kinetics of the sulfur redox reaction (SRR), and poor electronic and ionic cathode conductivities.[2] The use of defect-engineered catalysts, with tunable surface chemistry and electronic properties, as cathode additives in LSBs is a promising strategy to accelerate the Li-S redox reactions and thus promote LSB performance. In contrast to earlier research that predominantly concentrated on how defects influence the electronic density of states, the present work explores the impact of defects in modulating electronic spins and how these changes in spin configuration influence the macroscopic adsorption properties and activity of the catalytic additive.

Methods

In this study, a defect engineering strategy was used to tune the electron spin state of an SRR electrocatalyst. This strategy was showcased by introducing controlled amounts of cation vacancies within ultrathin CoSe nanosheets through plasma etching. Atomic resolution aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) was used to gain in-depth insights into the spatial distribution of Co vacancies. 3D atomic models were obtained by using Rhodius and the corresponding AC-HAADF-STEM image simulations obtained by using STEM-CELL software.[3-4] XRD, EXAFS, XPS, Raman spectroscopy, XMCD, DFT calculations, EPR, in situ XRD combined with electrochemical test were conducted.

Results

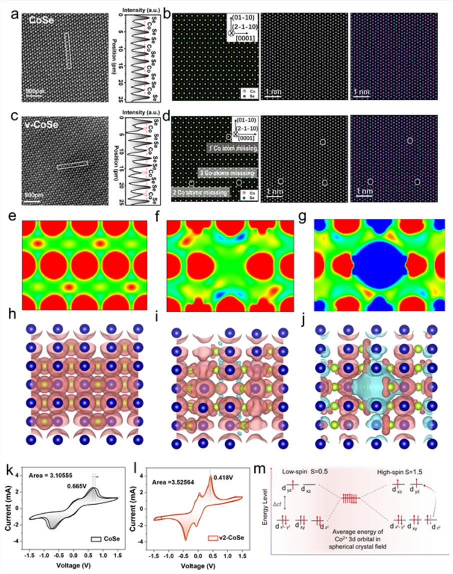
Vacancies were also indirectly evidenced by an increase of disorder and reduced lattice spacing, Co-Se bond length, and Se coordination number using XRD, HRTEM, EXAFS, XPS, and Raman spectroscopy. XANES and XPS spectroscopy further showed an increase in the average oxidation state of cobalt with the introduction of vacancies and EELS pointed to a higher occupation of Co 3d states in v-CoSe. Beyond modifying the structural parameters and electronic state occupation, the presence of vacancies resulted in a polarization of the 3d electron spins as evidenced by an increase in the intensity of the satellite peak in the Co 2p XPS spectra, a strong Co dichroism signal obtained by XMCD and magnetic measurements that confirmed a large moment per Co ion of 2.8 muB in v-CoSe. EPR spectroscopy further confirmed the generation of additional electrons with unpaired spins by the introduction of Co vacancies.

DFT calculations showed these spin-polarized unpaired electrons to be easily transferred from v-CoSe to polysulfide. Computational results showed that the d band center shifts toward the Fermi level with the introduction of vacancies, which involves that electrons are more prone to disperse in the high-spin configuration. The altered spin configuration results in a swift transferability of additional unpaired electrons to the polysulfide. DFT calculations also showed v-CoSe to have significantly higher lithium polysulfide adsorption energies and to decrease the polysulfide stability upon adsorption, thus enhancing both polysulfide adsorption and conversion activity. Besides, computational results showed the modified spin configuration to result in a more favorable thermodynamic reduction process, particularly for the transition from soluble polysulfide to solid Li2S that showed a lower nucleation energy barrier.

Experimental measurements confirmed an enhanced adsorption of the lithium polysulfide on the v-CoSe surface. Symmetric cells showed v-CoSe to provide a low polarization voltage and sharper and more intense redox peaks. In situ XRD showed a very rapid and complete transformation of S8 and a high lithium polysulfide redox activity in v-CoSe. EIS analyses showed v-CoSe to be characterized by a low SRR activation energy, particularly for the liquid-solid conversion stage. Besides, the presence of vacancies resulted in promoted Li2S nucleation, reduced LSB polarization voltages, and higher Q2/Q1 ratios. v-CoSe cathodes not only demonstrated excellent electrocatalytic properties but also outstanding LSB electrochemical performance in terms of specific capacity, rate performance, and cycling stability, even at high sulfur loadings.
As a result, more uniform nucleation and growth of Li2S and an accelerated liquid-solid conversion in LSB cathodes are obtained. These translate into CoSe-based LSB cathodes exhibiting capacities up to 1089 mAh g-1 at 1C with 0.039% average capacity loss for 1500 cycles, and up to 5.2 mAh cm-2, with 0.16% decay per cycle after 200 cycles in high sulfur loading cells.

Conclusion
Overall, this study demonstrates the need for considering the electronic spin configuration in the design of electrocatalysts, particularly for developing robust LSBs. Thus, the spin engineering approach showcased here paves the way to the rational design of new generations of LSB cathodes based on defect-engineered SRR electrocatalysts, toward the development of a cost-effective LSB technology with market-ready potential.

Graphic:



Keywords:

AC-HAADF-STEM, battery, vacancy, spin polarization

Reference:

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