

Mechanistic studies of Li-O₂ batteries

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Li-O₂ are associated now with future high-energy storage devices. Li-O₂ is composed of porous cathode where oxygen reduction product is deposited during discharge, Li metal anode and aprotic electrolyte. There are three main obstacles limiting their capacity and cyclability and, hence, practical applications: 1) Li₂O₂ deposition inside of porous cathode, which can be nonuniform, 2) cathode material and electrolyte degradation due to superoxide species, 3) developed Li morphology during plating. To tackle these problems underlying mechanisms should be understood.

Li₂O₂ deposition inside of porous cathode has two different regimes: surface deposition and solution growth which managed by superoxide species stability in electrolyte solvent, which is higher for solvents with high donor number. In this case mesocrystal growth is observed which we studied in situ by X-ray and neutron scattering and XRD. In addition, pore filling was model to reveal conditions to avoid pore clogging.

Mechanistic studies of oxygen reduction, electrode and electrolyte degradation are discussed. Operation of Li-O₂ batteries includes reactions of molecular oxygen. In this case ambient pressure (AP) XPS is rather relevant tool to probe reaction mechanisms. First, we have developed model electrochemical cell for operando studies with solid electrolyte to exclude influence of electrolyte. As a positive electrode transferred graphene was used. This approach enables to observe electrochemical reactions and side chemical reactions separately using different discharge and charge regimes. We observed directly in O 1s spectra short-living superoxide radical species (oxygen reduction intermediate) and their reactions with electrode materials. In addition, different electrode materials were tested. Using the same cell, we find the way to evaluate solid electrolyte instability towards metallic lithium negative electrode and trace the formation of SEI. Second, we have studies side reactions with electrolyte by admitting solvent vapor. This approach allows us to reveal some reactivity even for relative stable solvents such as acetonitrile. Unfortunately, this kind of studies is technically limited for many solvents since they are not safe for the spectrometer. All in all, AP XPS enables important findings for Li-O₂ batteries especially in the case when adequate model system is used. At the same time the approaching to the realistic operation conditions requires additional efforts including technical issues.

Lithium plating - one of the critical processes in the desired high-energy lithium metal batteries - is accompanied by lithium whisker growth, which causes several problems that prevent the employment of metallic lithium anodes in rechargeable systems. They include low coulombic efficiency, electrolyte consumption, and the risk of short circuits, which can lead to thermal runaway of the battery. In recent years several strategies were suggested to mitigate whisker growth. The mechanism of this process, however, still lacks understanding. We reveal the importance of surface diffusion along grain boundaries in solid lithium. We show that, at first, the plating of lithium onto a lithium substrate is possible as bulk crystal growth with a planar crystallization front for the Li grains with oblique (nonperpendicular to the surface) grain boundaries. Further, the developed compressive stress makes lithium diffusion to the grain base unfavorable, and new grains nucleate at the surface. The latter are the cause of the whisker growth from their roots. These findings indicate that the control of grain-boundary diffusion and grain size and structure paves the way to overcome the nonuniform morphology of plated lithium.