Abstract

High-capacity battery systems are needed for further development of portable electronics and electric vehicles. Current lithium-ion batteries are getting close to their theoretical limitations, and this research is focused on new alternatives. One of them is the use of magnesium anode, desirable for its high volumetric capacity, relative safety, availability and price. Theoretically, pairing magnesium anode with an inorganic insertion cathode offers high voltages, while conversion cathodes boast high specific capacities. Realizing these theoretical promises is not simple, and a better understanding of the basic mechanisms is needed.

In the presented work, we have researched two manganese oxide polymorphs as potential insertion cathodes. Magnesium insertion into spinel and birnessite structure was investigated in aqueous and organic electrolytes. Structural changes were analysed with transmission electron microscopy. We confirmed the successful insertion of Mg into both structures. Severe structural degradation and transformation were detected in samples, influencing electrochemical responses of the cells.

Our work on conversion materials was focused on the Mg-S system. First, we investigated the proposed mechanism of sulfur reduction and determined the final discharge product. With *operando* techniques, we showed that the sulfur reduction proceeds through polysulfide formation during high-voltage plateau and the precipitation of the MgS as the final product in the low-voltage plateau. Precipitated MgS was found to be amorphous with tetrahedral coordination of Mg, resembling the wurtzite structure.

With obtained information and understanding, we tried to improve high polarisation and fast capacity fade of the system. The addition of Se to the S cathode did not significantly improve polarisation or capacity fading. Concentrated electrolytes, used to lower polysulfide solubility, only partially improved cycling stability.

Finally, we evaluated the influence of Cu current collector on the electrochemical properties of the Mg-S system. We confirmed that the presence of Cu decreases the polarisation and improves the stability by actively participating in redox reactions. With that, the energy density of such a cell is unattractive for commercialization.

With the presented research, we deepened our understanding of magnesium batteries and their fundamental issues. Hopefully, this insight will help us solve the remaining challenges preventing the practical application of the system.