Order and disorder in metal-ion battery materials

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Rechargeable batteries enable switching to “green” energy production and consumption making a decisive impact in electromobility and integration of renewable energy sources into electric grids. Steadily rising demands in increasing specific energy, durability and lowering cost of electrochemical energy storage devices inspired extensive search for improved positive electrode (cathode) materials for advanced metal-ion batteries. Rational design of the cathode materials requires understanding of the intricate relationships between their crystal and electronic structures, as well as their evolution in course of reversible (de)intercalation of the alkali cations and through extended number of charge and discharge cycles. As the intercalation-type electrodes rely on long-range cationic diffusion reckoning on availability of the cation migration pathways with low energy barriers, the presence, spatial distribution, concentration and atomic structure of point and/or extended defects, which can block the ionic transport, have huge impact on capacity and rate capability of the metal-ion batteries. Polyanion cathode materials demonstrate extremely complex chemistry and crystallography of defects leading to exchange of the alkali and transition metal cations as a result of the synthesis or formed upon electrochemical cycling. Antisite cationic defects, heterovalent anionic defects and order-disorder in the alkali metal sublattice will be considered in relation with the electrochemical capacity, cycling stability and a competition between the solid-solution and two-phase (de)intercalation mechanisms in A_2MPO_4F (A – alkali cation, M – transition metal) and $LiFePO_4$ polyanion cathodes. Cationic disorder in the layered $A_{1+x}M_{1-x}O_2$ oxide cathodes is believed to play pivotal role in voltage fade and voltage hysteresis. The degree of this disorder will be characterized at different spatial scales using a combination of diffraction techniques and aberration-corrected transmission electron microscopy, both in the pristine materials and in the materials at different states of charge. Finally, the relationships between planar defects, such as twin boundaries and stacking faults, and electrochemical properties of the hierarchically-structured layered oxide cathodes will be demonstrated.

Keywords*:* metal-ion battery, cathode, defect, structure, transmission electron microscopy

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