

CONDENSED MATTER SEMINAR

Thursday 23 November at 14:30

Simpkins Lee room

“Degradation in Li ion battery cathodes: A strong correlations perspective”

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Layered Li ion battery cathode materials are strongly correlated transition metal oxides, where static and dynamic correlations play an important role in the degradation and stability of these materials. In this talk we examine the effect of strong correlations on the structural and electronic stability of two popular Li ion battery cathodes, LiMnO₂ and LiNiO₂.

LiMnO₂ is a low-cost, low-toxicity, high safety, and environmentally friendly alternative to popular rechargeable lithium-ion battery cathode material LiCoO₂, however it undergoes degradation in the form of irreversible transformation from layered to spinel structure causing loss of capacity and voltage. Using ab initio dynamical mean-field theory we explore the electronic and magnetic states of layered Li_xMnO₂ as a function of x, the state-of-charge. The antiferromagnetic insulating state in LiMnO₂ has a moderate Neel temperature of T_N=296K in agreement with experimental studies. Upon delithiation the system proceeds through a number of states: ferrimagnetic correlated metals at x=0.92, 0.83; multiple charge disproportionated ferromagnetic correlated metals with large quasiparticle peaks at x=0.67, 0.50, 0.33; ferromagnetic metals with small quasiparticle peaks at x=0.17, 0.08. At moderate states of charge, x=0.67- 0.33, a mix of +3/+4 formal oxidation states of Mn is observed, while the overall nominal oxidation of Mn state changes from +3 in LiMnO₂ to +4 in MnO₂. The charge disproportionation in the system is correlated to

different quasiparticle peaks on different sites, and gives rise to the origin of the pathways leading to the observed layered to spinel irreversible structural transformation in LiMnO₂ [1].

LiNiO₂ has the highest voltages and capacities in layered Li-ion batteries but is prone to structural instabilities and oxygen loss via the formation of singlet oxygen. Using ab initio molecular dynamics simulations, we observe spontaneous O₂ loss from the (012) surface of delithiated LiNiO₂, singlet oxygen forming in the process. We find that the origin of the instability lies in the pronounced oxidation of O during delithiation, i.e., O plays a central role in Ni-O redox in LiNiO₂. For LiNiO₂, NiO₂, and NiO, dynamical mean-field theory calculations based on maximally localised Wannier functions yield a Ni charge state of ca.

+2, with O varying between -2 (NiO), -1.5 (LiNiO₂) and -1 (NiO₂). Predicted XAS Ni K and O K-edge spectra show excellent with experimental XAS, confirming the predicted charge states and that a shift in Ni K-edge energy primarily arises from changes in Ni-O bond lengths rather than the Ni charge state. The O₂ surface loss route observed here consists of 2 surface O•- radicals combining to form a peroxide ion, which is oxidised to O₂, leaving behind 2 O vacancies and 2 O₂⁻ ions: effectively 4O•- radicals disproportionate to O₂ and 2 O₂⁻ ions. Singlet oxygen formation is caused by the singlet ground state of the peroxide ion, with spin conservation dictating the preferential release of 1O₂ rather than 3O₂ in our AIMD calculations [2].

Ref.

[1] Hrishit Banerjee, Clare P. Grey, Andrew J. Morris, arXiv:2209.14682

[2] Annalena R Genreith Schriever, Hrishit Banerjee, Ashok S Menon, Euan N Bassey, Louis F Piper, Clare P. Grey, Andrew J. Morris; Joule 7 (7), 1623-1640, 2023

Host: Santanu Saha