Understanding the Effects of Cationic and Anionic Substitutions in Spinel Cathodes of Lithium-ion Batteries

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INTRODUCTION

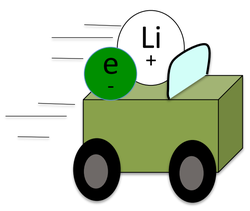
Why spinel cathodes?

Safety

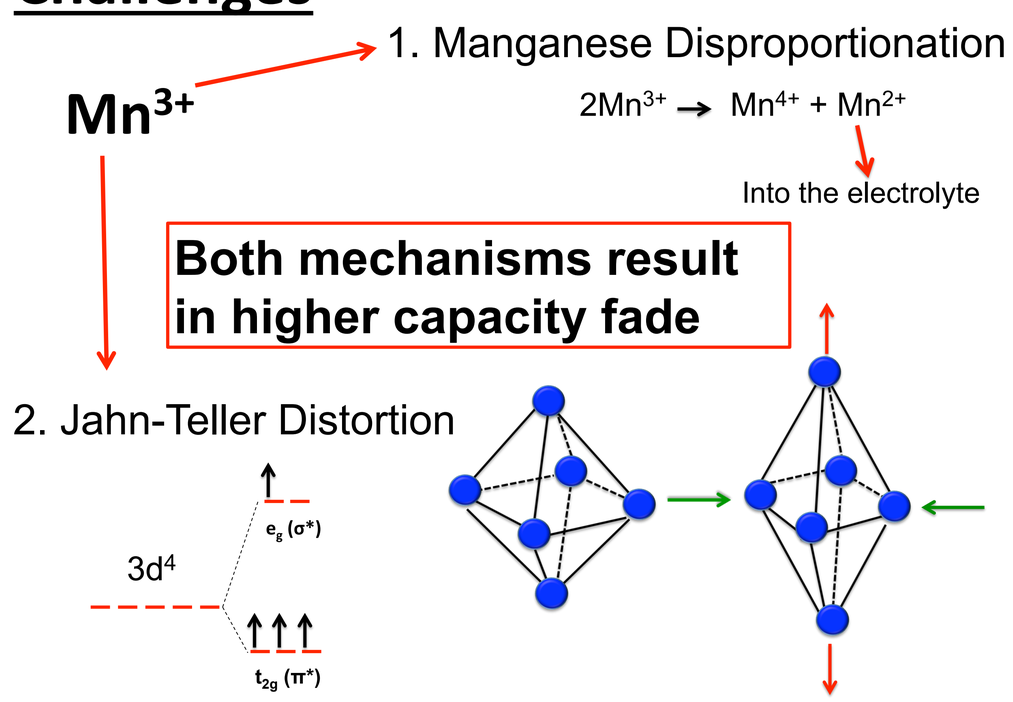
Mn Cost

Less toxic

Kinetics



Challenges



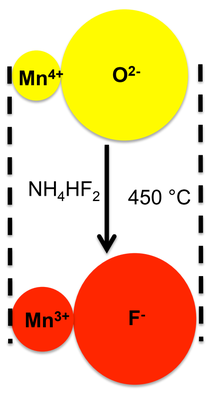
Objective

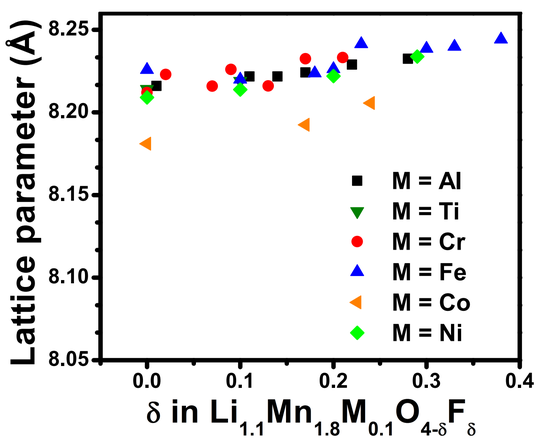
Previous research has proven cation substitution for manganese can improve the spinel cathode performance but at the expense of lower capacities due to the decreased concentration of Mn^{3+}. In addition, spinel cathodes have been fluorinated to overcome the decreased capacities of doped spinel cathodes.

A series of $Li_{1.1}Mn_{1.8}M_{0.1}O_{4-\delta}F_{\delta}$ and $Li_{1+x}Mn_{2-2x}M_xO_{4-\delta}F_{\delta}$ (M = Al, Co, Cr, Fe, Ni, Ti) oxy-fluoride spinels were made by solid-state reaction followed by a low temperature fluorination reaction. The purpose of this study was to link the basic chemical properties of the dopants (M) to the electrochemical performance, with hopes of providing simple prediction tools to guide the design of new battery materials. In addition, the amount of fluorination that causes phase impurities and adverse effects to the cyclability were determined.

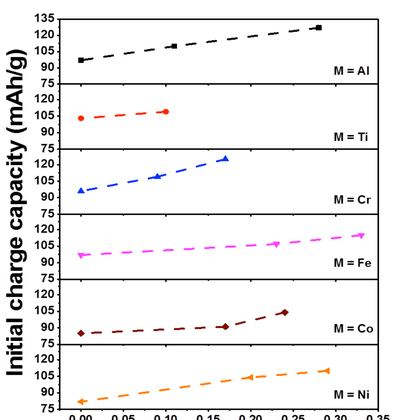
RESULTS

Evidence of fluorination

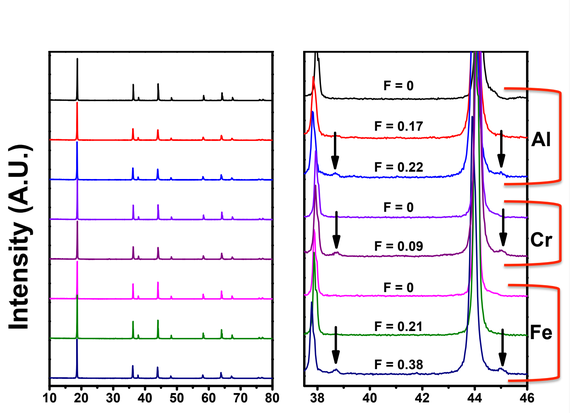




Combination of F^- and Mn^{3+} is slightly larger than O^{2-} and Mn^{4+}; therefore, an increasing lattice parameter is evidence of fluorine substitution for oxygen

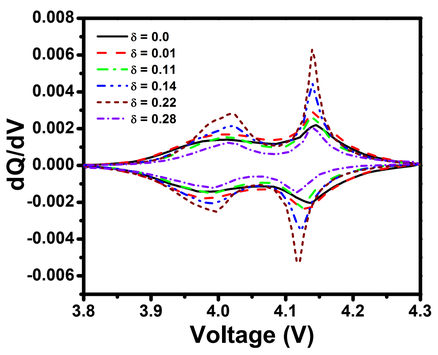


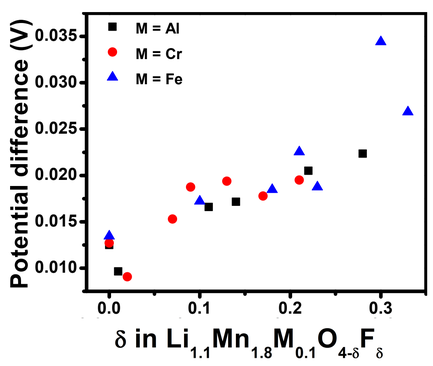
Increasing capacity is evidence of fluorine substitution and increased Mn^{3+} concentration

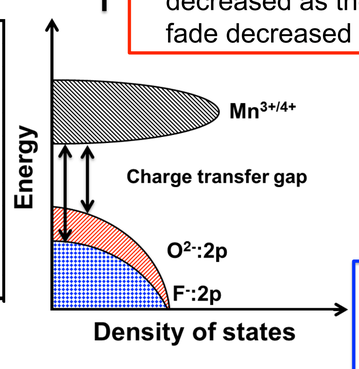


Arrows indicate lithium fluoride (LiF) impurity peaks; LiF impurity peaks generally occur at fluorine content of 0.2 or greater; Cr-doped samples were generally harder to dope with F^- and exhibited LiF peaks at lower F^- substitution

Kinetics

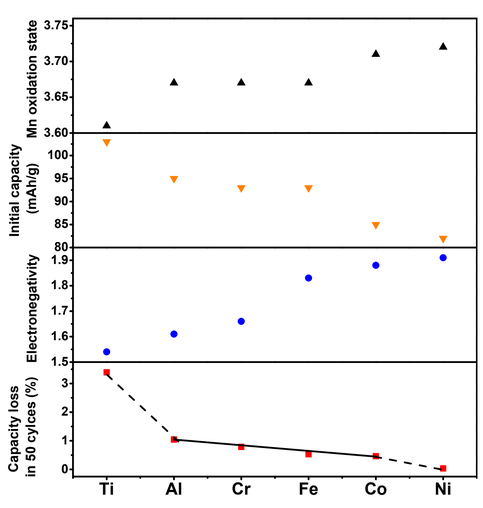


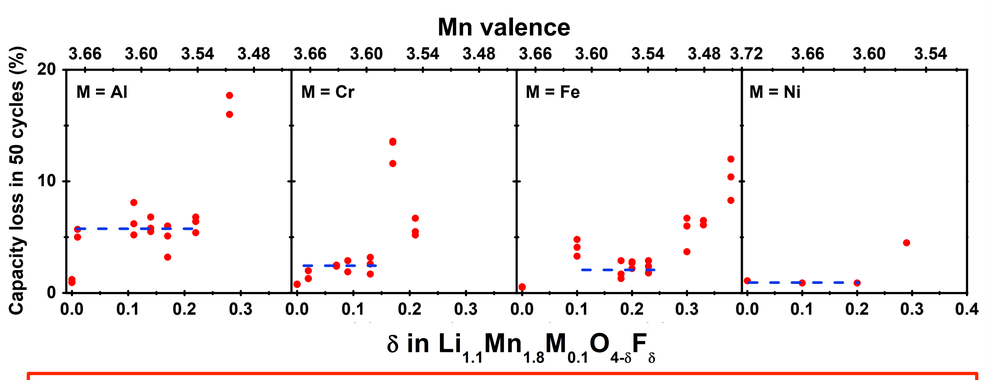




- Increased polarization occurs with increasing fluorine content in each series
- Worse kinetics suggested by increasing potential difference between redox peaks
- Kinetics worsen because of larger charge transfer gap upon fluorine substitution

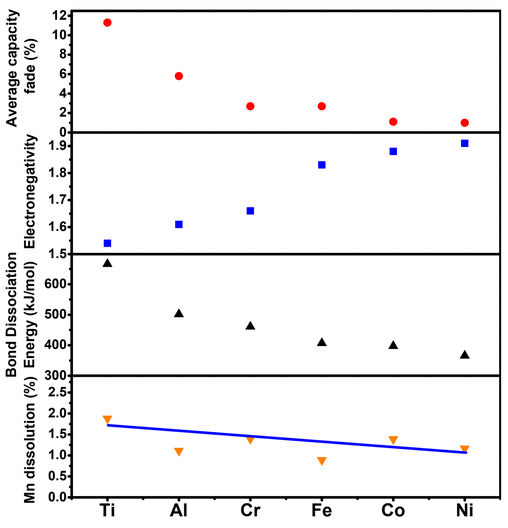
Cycling performance



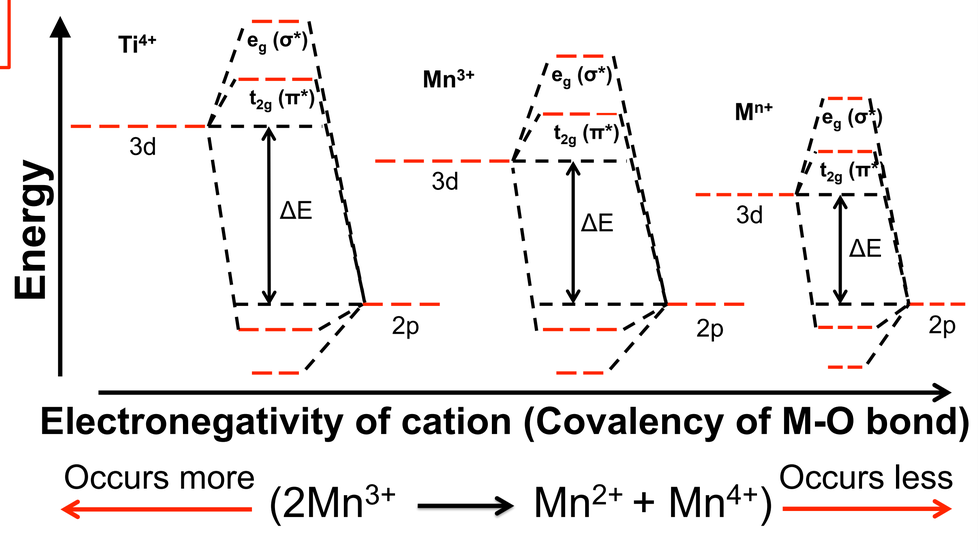


- Each series exhibited an "average capacity fade" (shown by blue line)
- "Average capacity fade" was different for each series
- A steady increase in capacity fade occurred at ~ 0.2 fluorine content
- Steady increase in capacity fade is attributed to Jahn-Teller distortion

"Average capacity fade" decreases with increasing electronegativity of doped cation in unfluorinated samples



- Average capacity fade decreased with increasing electronegativity of the doped cation in fluorinated samples
- Generally, manganese dissolution decreased as the average capacity fade decreased



A more covalent metal oxygen bond may suppress the amount of Mn^{3+} disproportionation and subsequently reduce the amount of capacity fade

Conclusions

1. The electronegativity of the dopant cations in the spinel oxide cathodes plays an important role on their cycling performance. By substituting more electronegative ions into the lattice for manganese, a more covalent metal-oxygen framework is formed. The increased covalency may suppress the amount of manganese dissolution and subsequently reduce the capacity fade.
2. As the fluorine content in the spinel lattice increases, the charge-discharge kinetics worsen as indicated by an increased separation between the potentials of the charge and discharge peaks. This is attributed to the decreasing covalence of the metal-oxygen framework caused by the substitution of more electronegative fluorine for oxygen.
3. At a fluorine content of ~ 0.2, the capacity fade experiences a steady increase. This is due to lowering the average manganese oxidation state close to 3.5+ and the consequent occurrence of dynamic Jahn-Teller distortion.
4. LiF begins to form an impurity at ~ 0.2 fluorine substitution for oxygen in the lithium manganese spinel cathode material.

Acknowledgements

IGERT Integrative Graduate Education and Research Traineeship