

**Mott Physics, Mixed Valence and Oxygen valence Changes
in the Modern Li-ion Batteries**

*High Performance $Li_2Ru_{1-y}Mn_yO_3$, ($0.2 \leq y \leq 0.8$) Cathode Materials for Rechargeable
Lithium-Ion Batteries: Their Understanding.*

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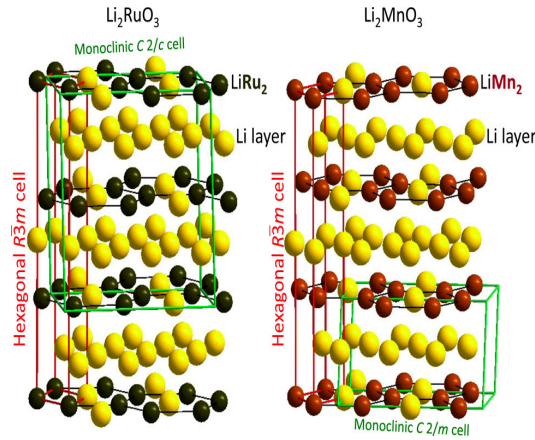
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Recommended with a commentary by Chandra Varma, University of California

Those of us who have been studying the strongly correlated quantum problems were intrigued when we learnt that $LiCoO_2$ which is a layered structure of CoO_2 , as is the CuO_2 structure in the high temperature cuprates, intercalated in between the layers is the prototypical anode material in the modern Li-ion batteries, on which we have become so dependent in the last decade. Doped $NaCoO_2$ with various amounts of hydration itself has been investigated for superconductivity. Of course the actual materials for battery cathodes are more complicated, using mixtures of various transition metals and oxides and phosphates and almost certainly other closely held knowledge. It feels good to know that a leading role in the ideas behind the modern Li-ion battery has been played by John Goodenough [1], whom we know to have contributed much to the magnetism and metal-insulator transitions in transition metal compounds and whose knowledge of the physics of correlations together with solid state chemistry appears to have played a decisive role.

Now chemists and physicists have begun to use techniques such as X-ray photomission spectroscopy and detailed x-ray and synchrotron diffraction measurements together with chemical techniques to probe the changes in the valence states, crystal structure, microstructure, as well as of-course the traditional electro-chemical studies, in various stages of the battery operation, charging, discharging and in recycling.

The actual battery compounds are complicated with inter-mixtures of different crystal structures for different components and various other structural and chemical inhomogeneities. The authors highlighted above chose to fabricate and investigate a simpler system which nevertheless has a comparable current capacity and voltage to the commercial Li-



ion battery. (There are three principal performance metrics in batteries beside of-course the cost: the voltage, the current capacity per unit-weight measured in milliamp-hours per gramme (mAhg^{-1}) and the number of charge-discharge cycles in which the performance is within say 50% of the initial values.) The idea is to mix the layered compounds of nearly the same structure Li_2RuO_3 and Li_2MnO_3 , shown in the figure taken from the paper listed above. These structures have Li by itself both in the layers as well as in the transition metal-oxide layers.

Through structural studies, it is found that the two components form a solid solution while preserving reasonably well the ordering of the LiM_2 layers. The structural studies are carried out in successive charging and discharging processes and reveal systematic changes in cycling. More than a Li per formula unit leaves the sample (de-intercalates) on charging with concomitant changes in valence (redox) of Ru and Mn, (4+) to (5+) and (4+) to (3+) respectively and changes in cell-volumes and width of diffraction peaks.

New and deeper insight is gained by x-ray photoemission in which the relative amount of Ru and Mn valence states and the amount of Li and oxygen in the sample in various stages of the battery operation is studied. As a typical physicist, poor in knowledge of chemistry, I found this part of the work easiest to understand. It brought forth issues that we are wrestling with in other contexts but aspect of those issues which can be answered by methods that have already been developed - sophisticated mean-field methods of handling correlations. The issues raised are those in charge transfer and mixed valence insulators. These are problems which cannot be handled well in Hartree-Fock theory and perhaps not too well in density-functional calculations. Of special interest is the necessary role that the

effective change in valence on Oxygen ($O(2-)$ to $O(-)$) appears to play. The calculational problem is to develop methods in which inhomogeneous compounds can be reasonably well treated as they struggle to maintain charge neutrality while their composition of highly correlated ions changes with $Li(1+)$ insertion and de-insertion which occurs with gradients in the sample leaving electrochemical potential gradients and corresponding mechanical gradients if not structural changes. It appears that given experiments of this kind and the calculational methods they may inspire, we may understand batteries. Understanding however is not by itself enough for creating new and better energy storage compounds.

[1] For a review of some of the work by Goodenough and collaborators, see J.B. Goodenough and K-S Park, J. Am. Chem. Soc. (2013); <http://pubs.acs.org>