The Origin of the Oxygen Redox Activity in Layered and Cation-Disordered Li-Excess Cathode Materials

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Oxygen redox enables very high capacity Li-excess cathode materials, leading to unprecedented energy density.

Extra capacities of Li excess materials that cannot be provided by the transition metal (TM) redox activities are explained by the oxygen oxidation.
The O redox mechanism was however controversial, preventing rational design of high capacity cathode materials with optimum O redox activity.

O charge transfer by covalency in LiCo$_x$Al$_{1-x}$O$_2$

Formation of peroxo-like species (O$_2^{2-}$) in Li$_2$Ru$_x$Sn$_{1-x}$O$_3$

Oxygen hole localization in Li$_x$Ni$_{1-x}$O

Ceder et al., Nature 392 (1998) 694


Tarascon et al., Nat. Mater. 12 (2013) 827

It is commonly believed that TM-O bond covalency leads to the extra capacity beyond TM redox capacity in Li-excess materials.
Conventional view of M-O bonding

- M orbital
- O orbital
- antibonding "M" state
- bonding "O" state
- regular redox states

Voltage

Energy
Oxygen electrons also participate in a redox process because some portion of antibonding state actually comes from oxygen electrons due to the covalent nature of M-O bonding.
M-O covalency does NOT increase capacity.

The number of electrons stays same at regular redox states regardless of O contribution, which were already counted into TM redox capacity. Therefore, oxygen contribution to antibonding state by covalency cannot lead to extra capacity beyond so called TM redox capacity.
Covalency actually makes oxygen redox more difficult.

Covalency is not the source of extra capacity through oxygen redox!!
Instead, less covalent makes oxygen redox easier.

What makes O states less stable?
To resolve such controversy, it is important to understand the effect of local environments on the oxygen electronic state.

Stoichiometric layered Li-M oxides (LiMO$_2$)

Li-excess layered Li-M oxides (Li$_{1.2}$M$_{0.8}$O$_2$)

Li-excess cation-disordered Li-M oxides (Li$_{1.2}$M$_{0.8}$O$_2$)
Prediction of the oxygen redox activity requires novel computational methodology beyond simple GGA or GGA+U.

Our advanced DFT (optimized HSE hybrid functional) method predicts accurate electronic structure as well as voltage profile of LiCoO$_2$. 

A model study on the effect of local environment around oxygen ion on the electronic state in layered Li-TM oxides

Model system - Li/Ni-mixed LiNiO$_2$

LiNiO$_2$: one of the most studied materials and the basis for many important derived compositions

Li/Ni cation mixing: various local environments of oxygen ions

1 pair of Li/Ni site exchange in Li$_{12}$Ni$_{12}$O$_{24}$
Various environments around oxygen in Li/Ni-mixed LiNiO$_2$

In Li/Ni-mixed LiNiO$_2$, there are three major local environments for oxygen: oxygen coordinated with (a) four Li and two Ni, (b) three Li and three Ni, and (c) two Li and four Ni.
pDOS on an oxygen ions clearly shows the difference in the oxygen electronic states by the local environment.

The electrons bound to an oxygen ion in the local Li-excess environments are energetically less stable than electrons bound to the other types of oxygen ions.

This labile electron along Li-O-Li configuration will be easier to be extracted than the electron from O bond states.

O oxidation occurs from these O 2p electrons along the Li-O-Li configurations in both Li-excess layered and cation-disordered cathode materials.

The oxygen oxidation in these Li-excess materials accompanies the electron extraction along the Li-O-Li configuration, leading to extra capacity beyond TM redox capacity.
O oxidation along the Li-O-Li configuration is universal in all the lithium excess layered and cation disordered materials.

The oxygen oxidation in these Li-excess materials accompanies the electron extraction along the Li-O-Li configuration, leading to extra capacity beyond TM redox capacity.

Lack of hybridization makes oxygen electrons in the Li-O-Li states high in energy (labile).

Hybridization of O 2p orbitals with M d/s/p orbital stabilized the (bonding) O 2p states.

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Lack of hybridization along the Li-O-Li configuration makes to O 2p electrons along the direction labile (unstable).

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Seo†, Lee†, Urban, Malik, Kang, Ceder, Nature Chem. (2016)
Li-O-Li oxidation leads to extra capacity in Li-excess materials.

Two different oxygen charge transfer upon delithiation in Li-excess materials:

1. **from the hybridized TM-O states (so called covalency):**
   - **cannot add extra capacity** beyond the TM redox capacity
     - \( e_g^*, t_{2g} \): already counted as TM redox capacity
     - \( t_{1u}^b, a_{1g}^b, e_g^b \): too stable to be oxidized

2. **from the Li-O-Li states (pure oxygen state):**
   - **can add extra capacity** beyond TM redox capacity because they are independent oxygen states

The oxygen oxidation from unhybridized O 2p states along Li-O-Li configurations is the origin of the extra capacity in the Li-excess materials.

Seo\(^\dagger\), Lee\(^\dagger\), Urban, Malik, Kang, Ceder, *Nature Chem.* (2016)
Summary

1. Covalency/Hybridization between the TM and oxygen does not create extra capacity beyond TM redox capacity.
Thank you very much!!

This presentation is available at http://ceder.berkeley.edu/
Dong-Hwa Seo et al., Nature Chem., 8 (2016) 692

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The Li-O-Li configuration results in unstable O electrons in Li₂MnO₃. The electrons along the Li-O-Li configuration in Li₂MnO₃ contribute to the large pDOS of the oxygen ion near below the Fermi level.
Oxygen oxidation occurs from “unhybridized” O 2p states along the Li-O-Li configurations in Li-excess materials.

Li-excess cation-disordered oxide

\[
\begin{align*}
\text{Li}_{1.25}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{O}_2 \\
\text{Li}_{0.75}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{O}_2 \\
\text{Li}_{0.25}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{O}_2 \\
\end{align*}
\]

Theoretical capacity based on Mn$^{3+}$/Mn$^{4+}$

Theoretical capacity based on Li content


Benchmarking Hybrid functional to experimental band gap

Density of State (DOS) of MO (M = Mn, Ni, Co)

- HSE mixing parameters can be adjusted for oxides to experimental band gaps. [S. Han et al., Curr. Appl. Phys. 11 S337 (2011)]
- Density of State (DOS) of transition monoxides with HSE06 and optimal mixing parameters are in better agreement with experimental results than those with GGA and GGA+U.
- \( G_0W_0 @ \text{GGA+U} \) band gaps agree well with experimental values, suggesting that it can be used as a reference in cases when no experimental band gap has been reported.

Simple way to obtain optimal mixing parameters

The band gaps increase linearly with the amount of exact HF exchange energy within $0 \leq \alpha \leq 0.3$. Thus, the optimal mixing parameter can be obtained by comparing a reference band gap with the linear interpolated band gap between GGA ($\alpha=0$) and HSE06 ($\alpha=0.25$).
Optimal mixing parameters of various Li-excess materials

We used optimal mixing parameter for each Li-excess compound.
Competition between TM redox and oxygen redox

Ni redox based Li-excess materials

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\[
\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 - 0.4 \text{ Li}
\]
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```
\[
\text{Li}_{0.8}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2
\]
```

Oxygen ions start to get oxidized before full oxidation of Ni\(^{2+}/\text{Ni}^{4+}\)

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\[
\text{Li}_{1.16}\text{Ni}_{0.33}\text{Ti}_{0.42}\text{Mo}_{0.08}\text{O}_2 - 0.66 \text{ Li}
\]
```

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\[
\text{Li}_{0.5}\text{Ni}_{0.33}\text{Ti}_{0.42}\text{Mo}_{0.08}\text{O}_2
\]
```

Mn redox based Li-excess materials

```
\[
\text{Li}_{1.25}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{O}_2 - 0.75 \text{ Li}
\]
```

```
\[
\text{Li}_{0.5}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{O}_2
\]
```

Oxygen ions start to get oxidized after full oxidation of Mn\(^{3+}/\text{Mn}^{4+}\)