TIMES for us: Theoretical Interpretation of the Mechanism and Electron States

- *Needs of RIXS theory on "Oxygen Redox"*

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Jinpeng Wu, Ruimin Qiao, Wanli Yang (ALS)

“Oxygen Redox”: the key & the hope

nature materials ARTICLES
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nature energy ARTICLES

“useful” “Oxygen redox”

- ***High electrochemical potential***
  - *Otherwise, useless!*
- ***Reversibility (stability)***
  - *Otherwise, useless!*

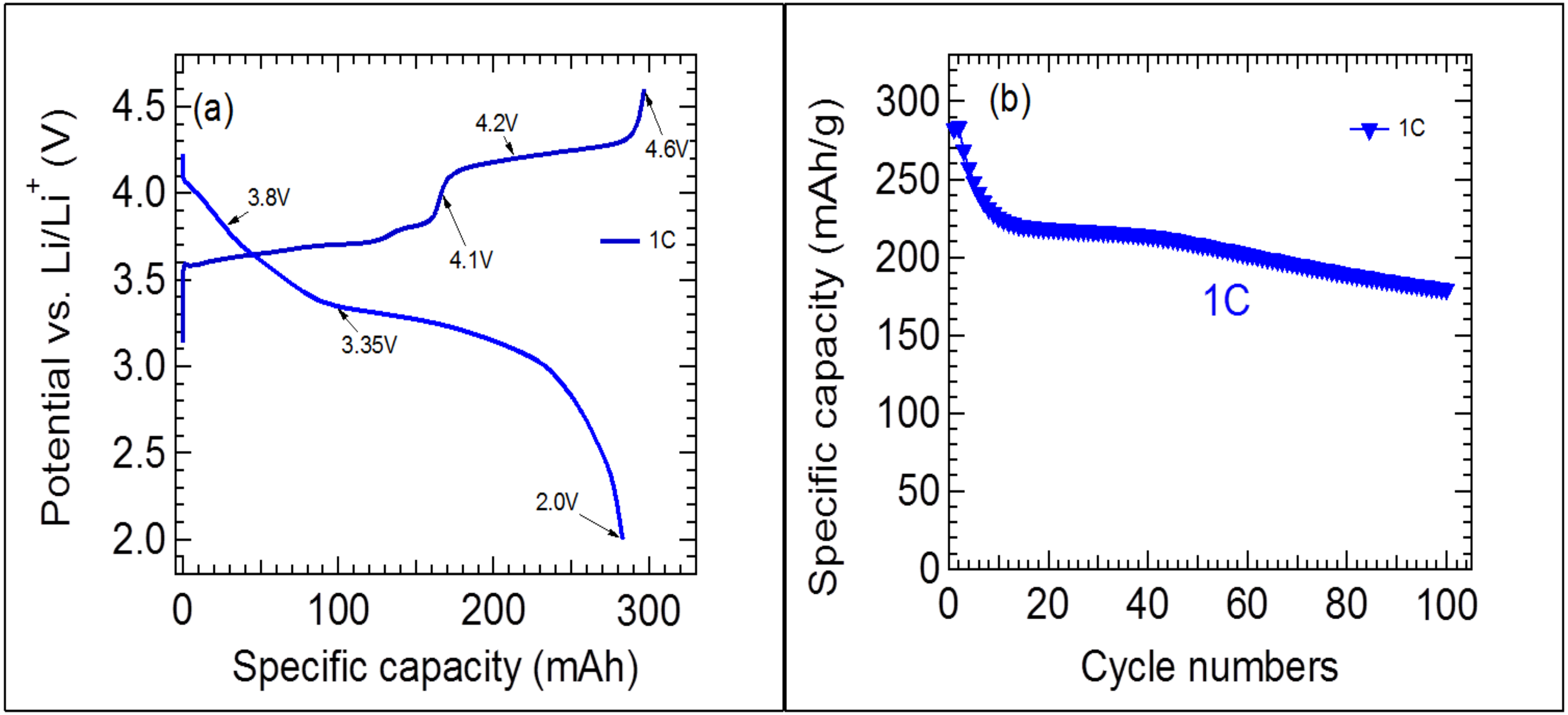
Anionic redox processes for electrochemical devices

A. Grimaud, W. T. Hong, Y. Shao-Horn and J.-M. Tarascon

dimers in high-capacity layered oxides for Li-ion batteries

Eric McCalla,[1,2,3,4] Artem M. Abakumov,[5,6] Matthieu Saubanère,[2,3,7] Dominique Foix,[2,3,8] Erik J. Berg,[9] Gwenaelle Rousse,[1,3,10] Marie-Liesse Doublet,[2,3,7] Danielle Gonbeau,[2,3,8] Petr Novák,[9] Gustaaf Van Tendeloo,[5] Robert Dominko,[4] Jean-Marie Tarascon[1,2,3,10]*

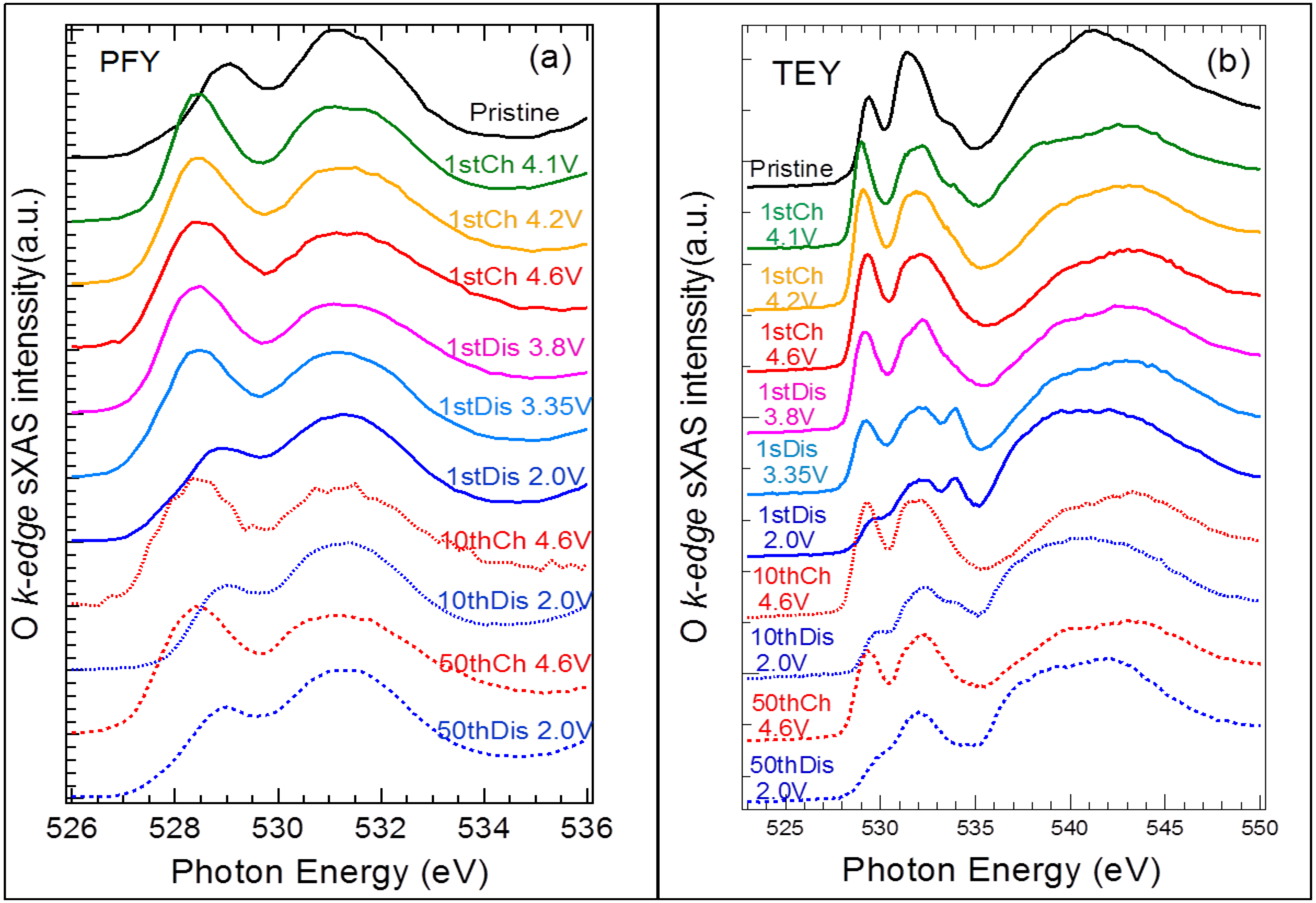
Electrochemical performance / Potentials of Li_2RuO_3



- Good electrochemical performance
- First discharge capacity: 290mAh/g

- Kehua Dai (2016)

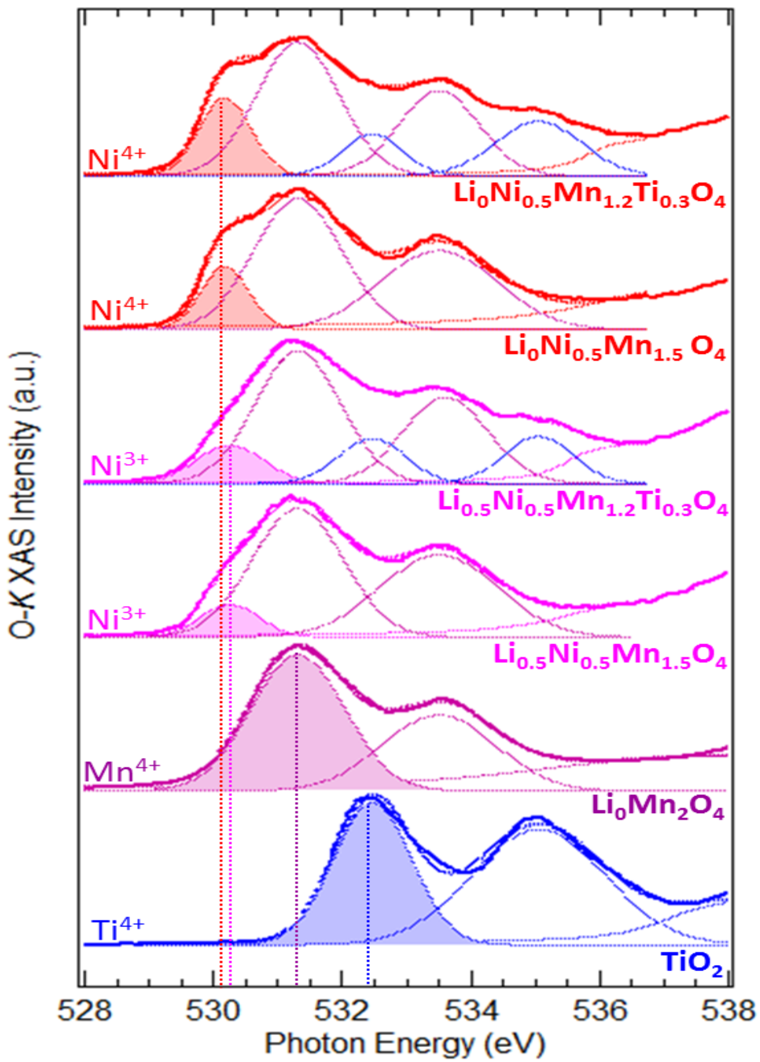
O-K sXAS, PFY & TEY

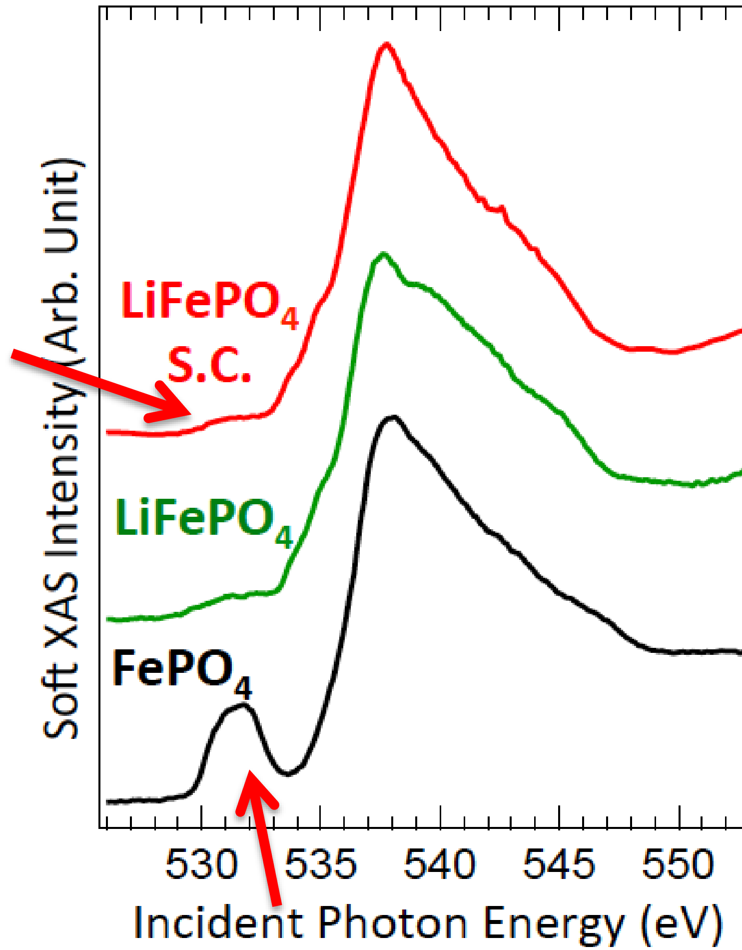


- "Pre-edge" features reflect the redox of *Transition-metals*!

- Zengqing Zhuo (2016)

*O-K sXAS "pre-edge" features: Transition-metal oxygen **hybridization***





***Lineshape**: TM redox*

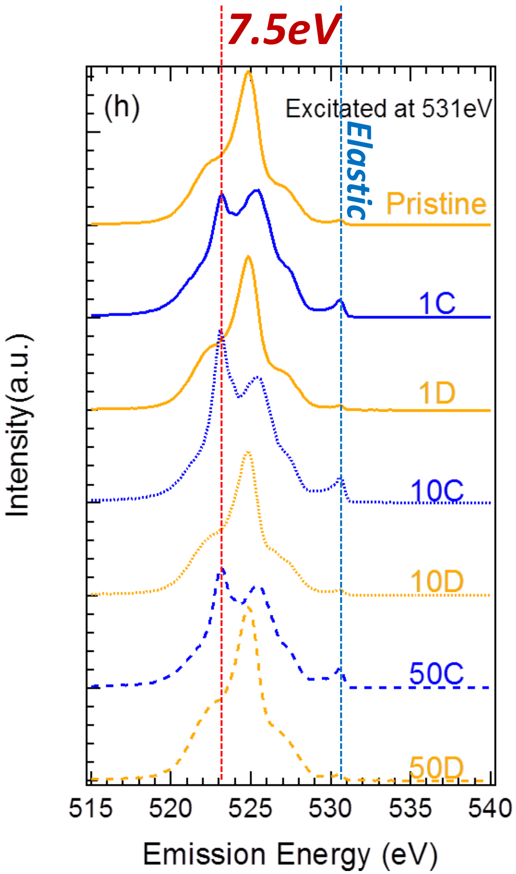
- Ruimin Qiao (2015)

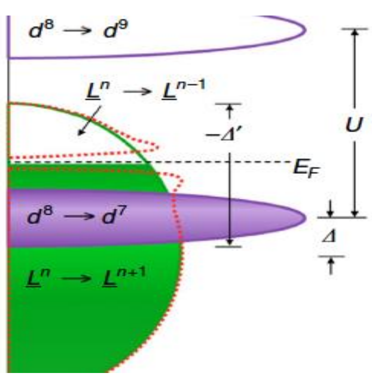
- Samples from General Motors

***Intensity**: hybridization strength*

Liu et al, PCCP 17, 26369 (2015)

More specific: What we need from theory?





The *7.5eV energy loss feature in RIXS*!

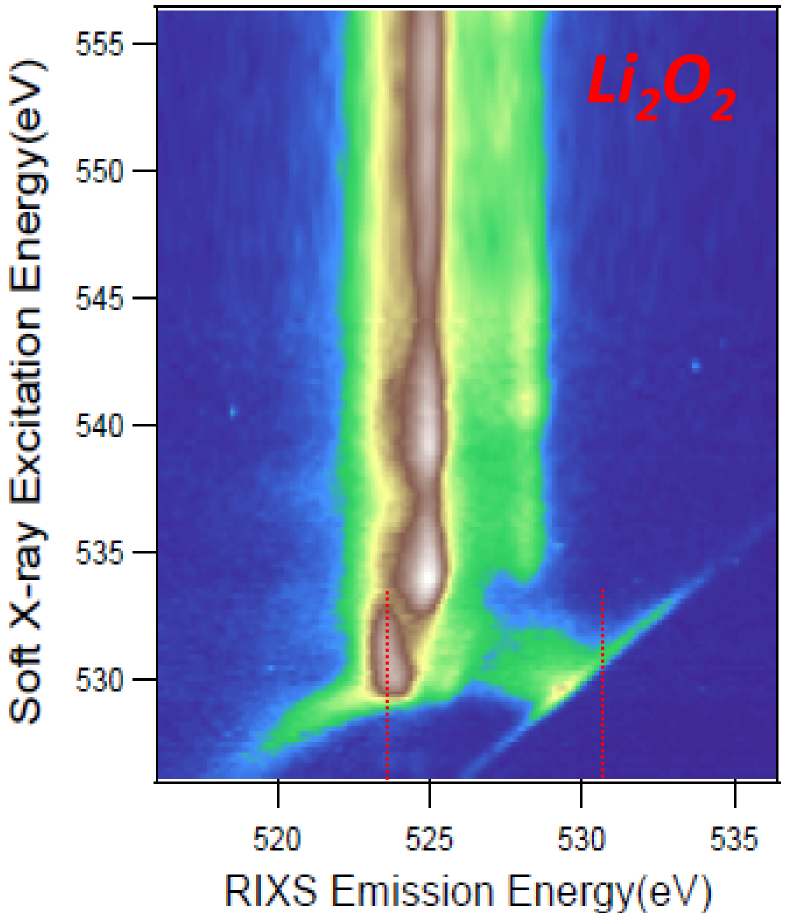
- Experimental evidence of the relevant (high potential + reversible) "oxygen redox" in bulk materials.

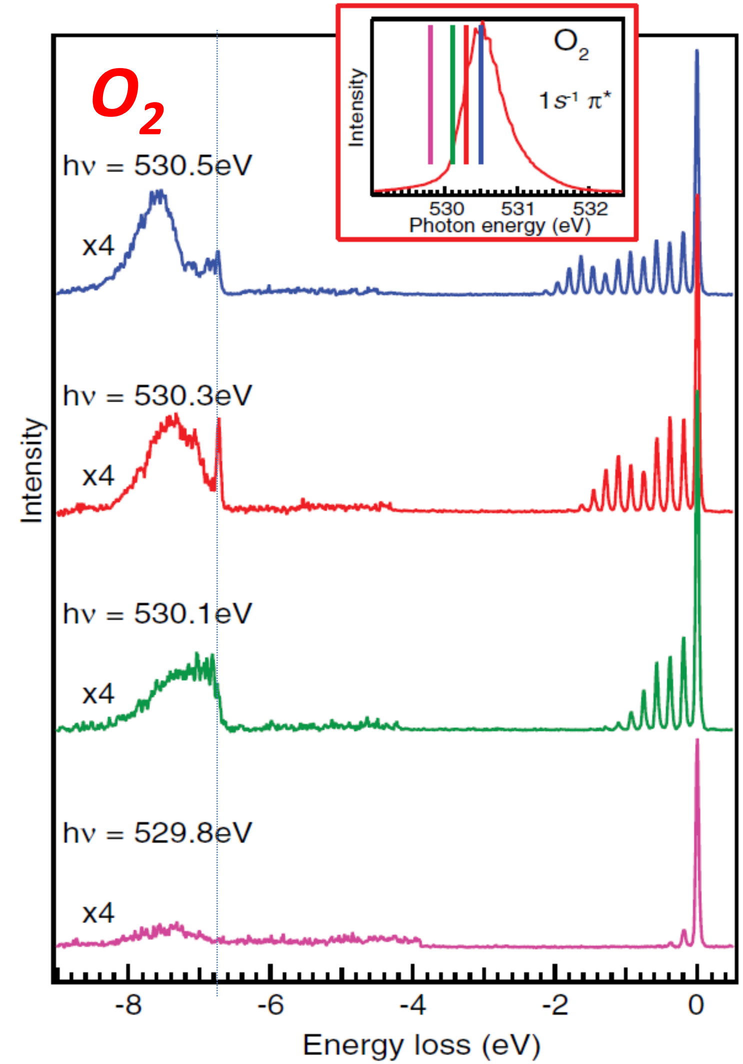
- ***Technically***, need RIXS interpretation with *contrast of lithiated and delithiated systems*.
  - ➢ General physics model, e.g., U_{pp}

- ***Ultimate goal***: a *molecular level scenario* to clarify the nature of "oxygen redox"
  - Peroxides?
  - "Li-O-Li" labile states?
  - Localized O holes?

➢ ***Conditions & Controllability of "oxygen Redox"***

Experimental Hints?





Hennies et al., PRL 104, 193002 (2010)

(6.5-8 eV: $B'^3\prod_g$ states)

What we guess (experimental):

- “extra” unoccupied states compared with O^{2-}, i.e., ***oxygen is indeed oxidized!***
- “THE” RIXS feature is likely from the combination of ***1) & U_{pp} effect!*** (***Tom’s talk***)