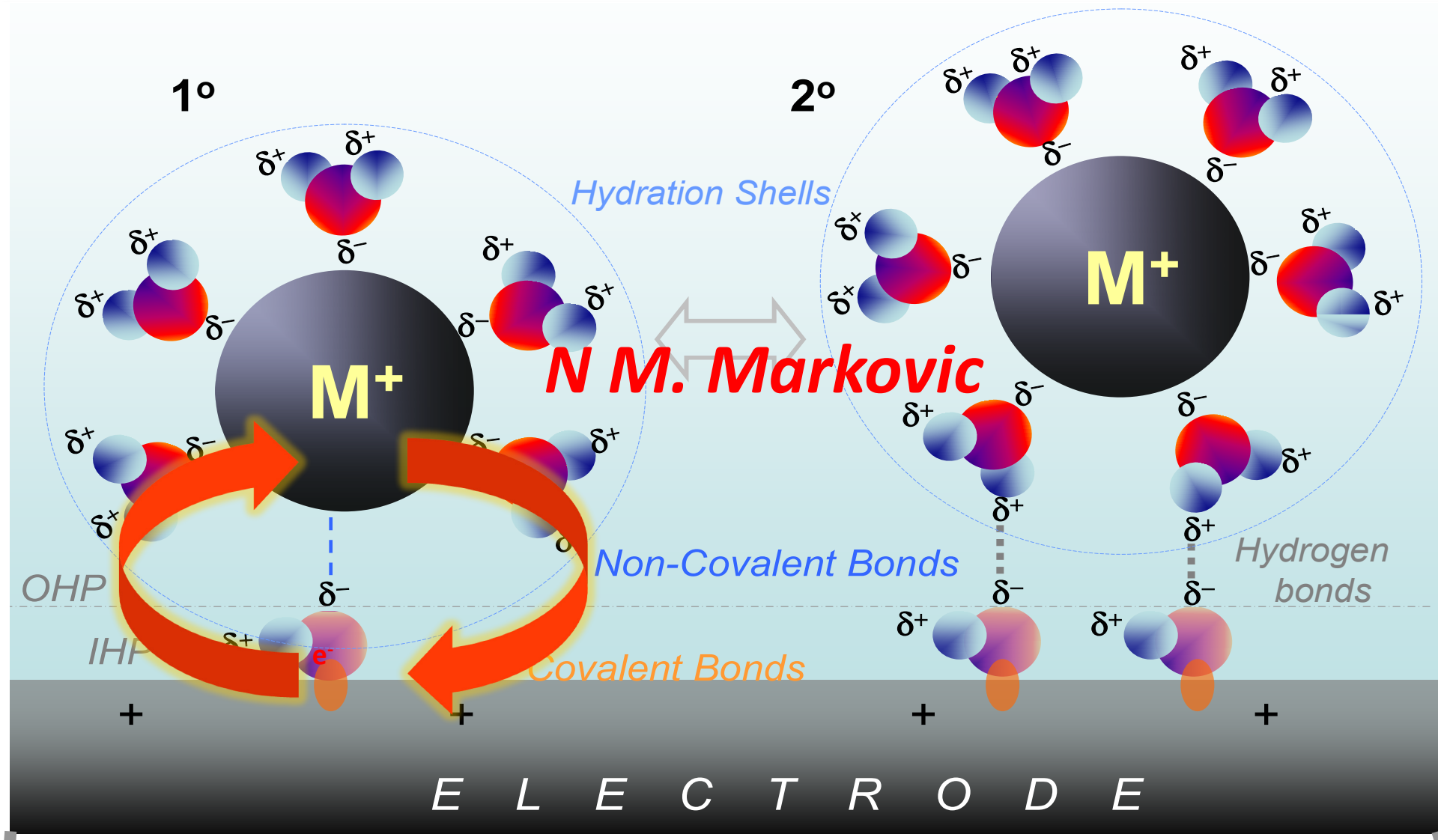
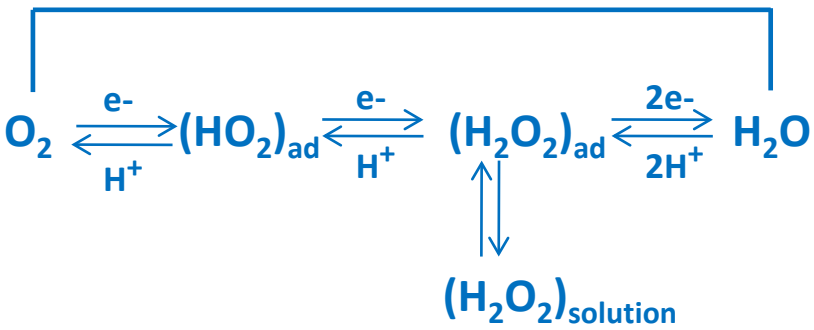
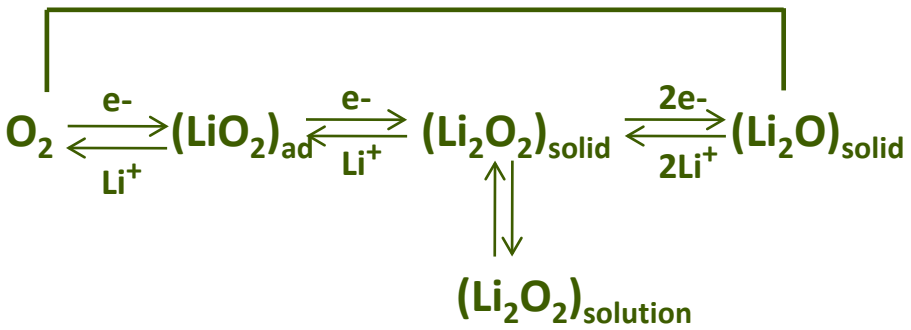
Li-air
Just a Dream of Future Reality



Water cycle



Lithium cycle



Use the knowledge from the water cycle to understand the lithium cycle

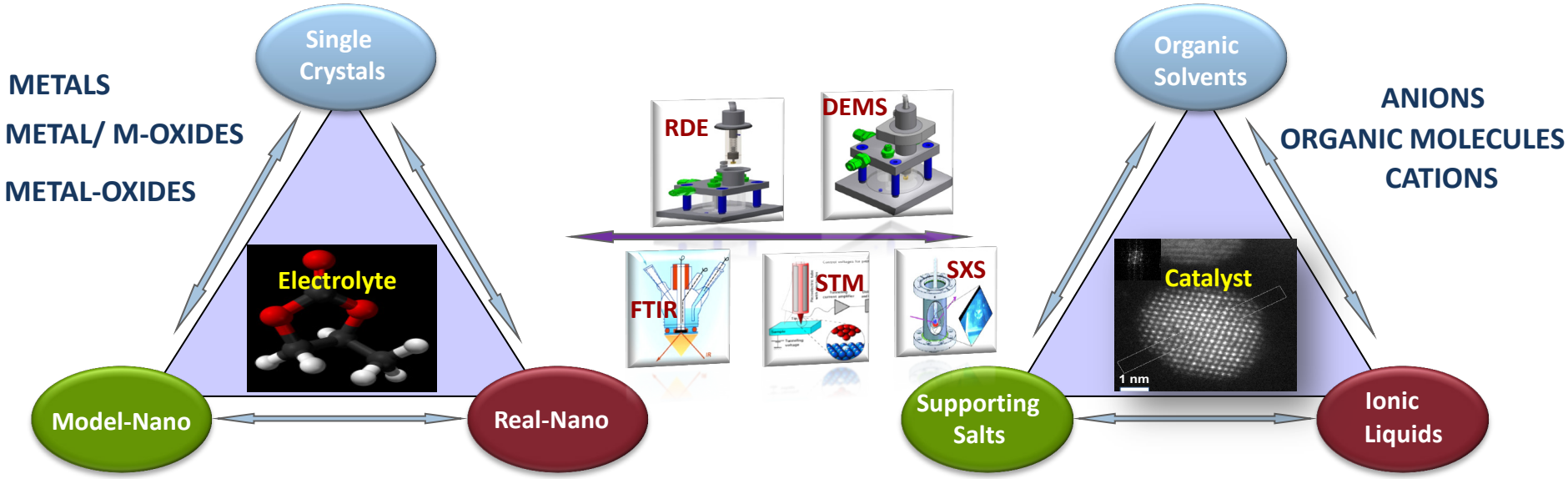
What I (think) know

- Reaction Pathway: serial via H_2O_2 formation
- Intermediates : O_2-, HO_2-, H_2O_2 , etc.
- Spectators : H_{upd}, OH_{ad}, anions
- H_2O_2 :
  - In-situ monitoring
  - Oxygen-radicals "attack" membrane
- Catalysts:
  - ORR: optimize Θ_s and ΔG_i
  - OER: optimize charge transfer and ΔG_i
- Stability of cathode (ORR) and anode (OER)

What I would like to know - DREAM

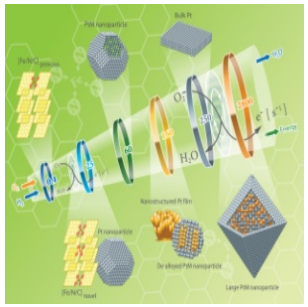
- Reaction Pathway?
- Nature of intermediates and products?
- Interaction with solvents?
- Solvation of Li^+?
- Any role of catalysts ?
- Stability of materials?
- ????????????

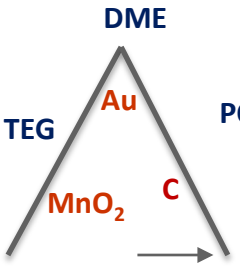
(Surface) Science Approach-Lithium Cycle

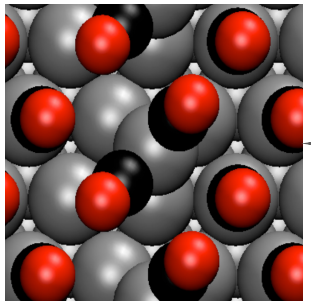


In-situ methods for probing structure function relationships and stability of electrolytes

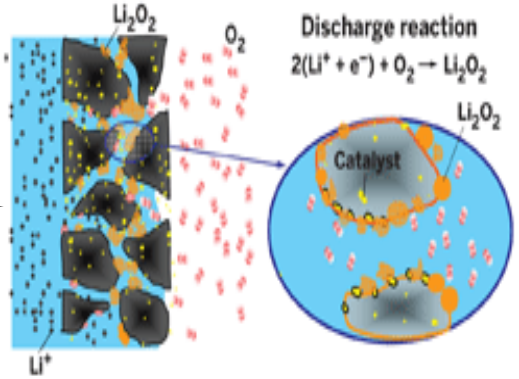
ACTIVITY, SELECTIVITY AND STABILITY MAPPING





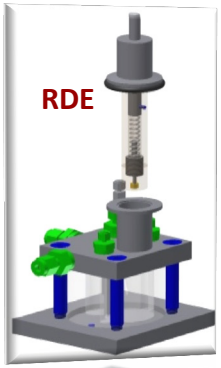


knowledge



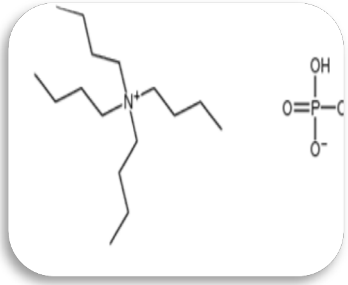
Experiment | Theory/Modeling | Metal-Air Batteries

Single crystals: ORR/OER in DME without Li^+



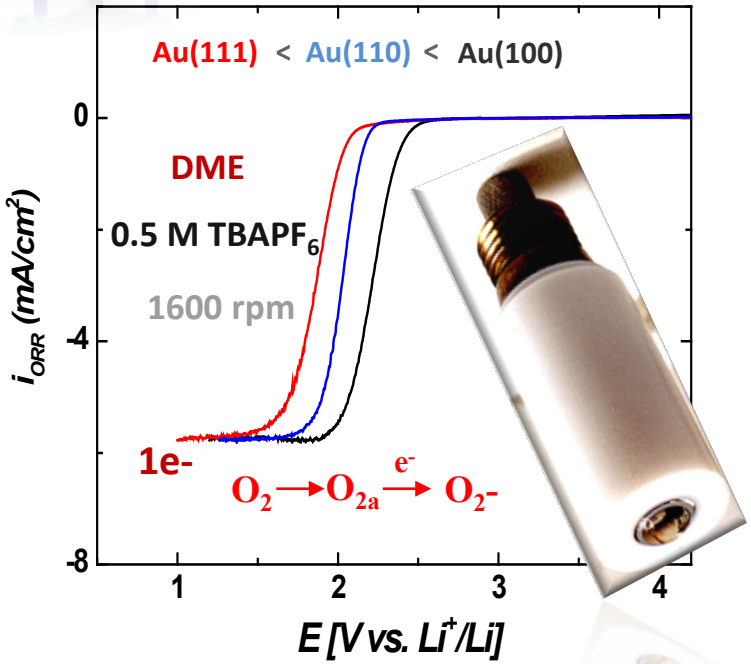
Superoxo (electro)chemistry

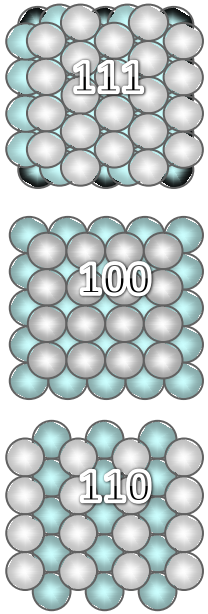
$$O_2 \xleftrightarrow{e^-} O_{(2ad)} \xleftrightarrow{e^-} O^-_{2(ad)} \longleftrightarrow O^-_{2(sol)}$$



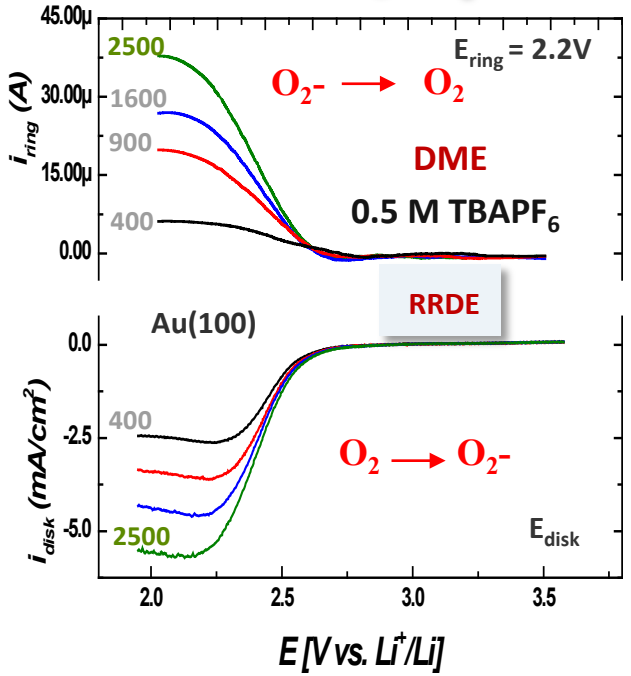
$TBAPF_6$

Structure sensitivity



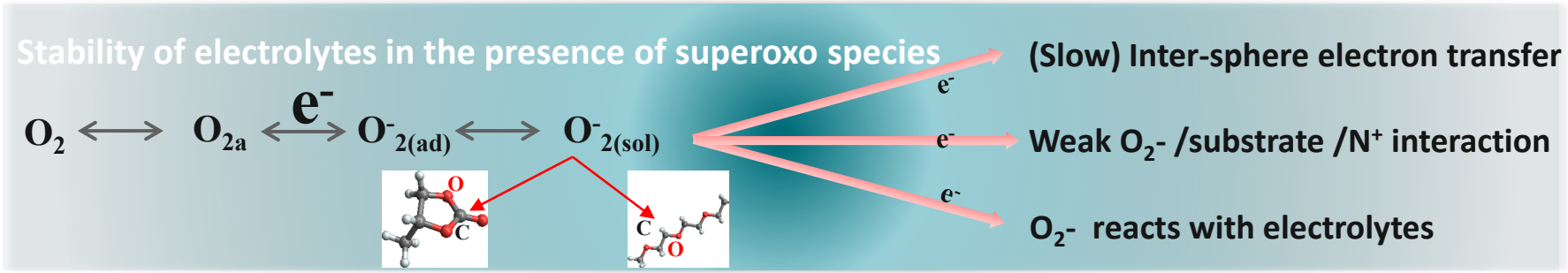


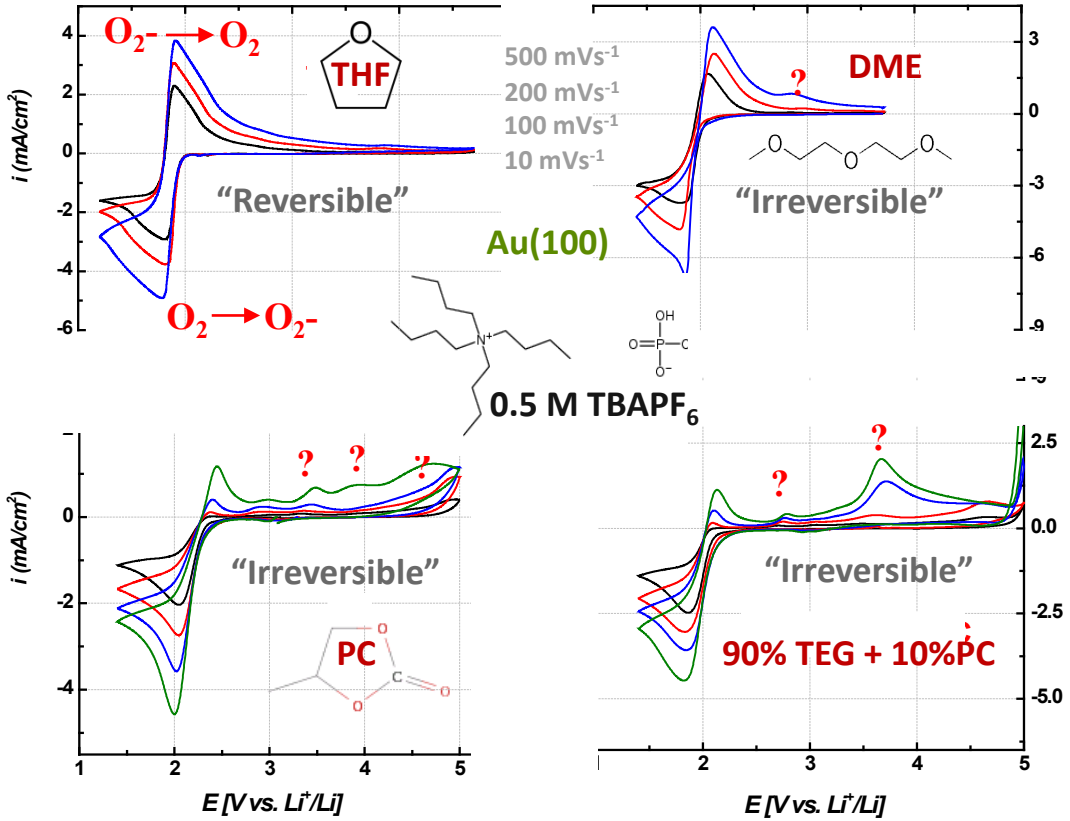
"Caching" O^-_2



- O_2- formation is catalytic reaction
- O_2- is detectable in organic solvents

Superoxo (electro)chemistry without Li^+

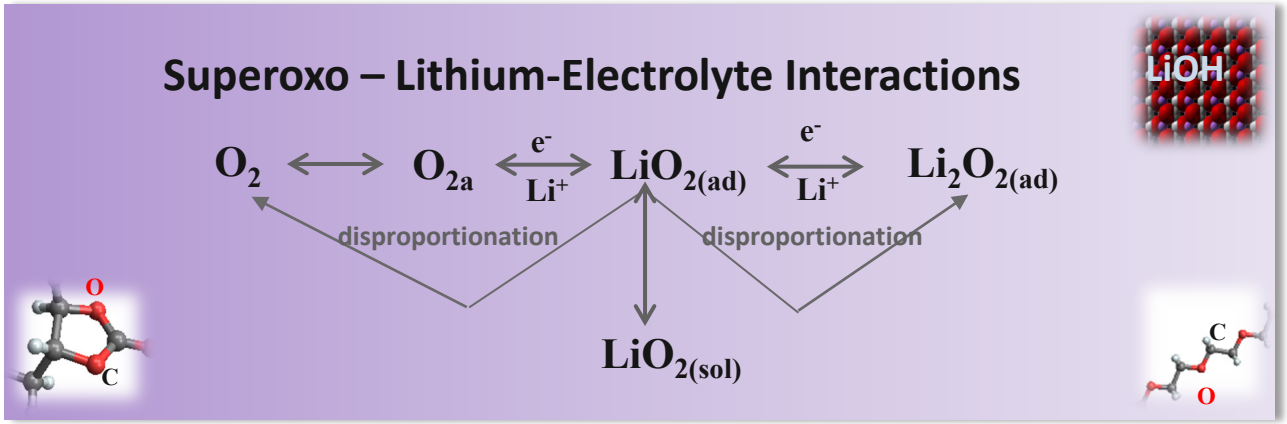




- Highly reversible in environments with limited or no reactivity; THF and $TBAPF_6$
- Irreversible in electrolytes "opened" for O_2- nucleofilic attack
- Multiple oxidation peaks: oxidation of electrolyte fragments
- Trends in stability:
  DME > TEG ≥ PC

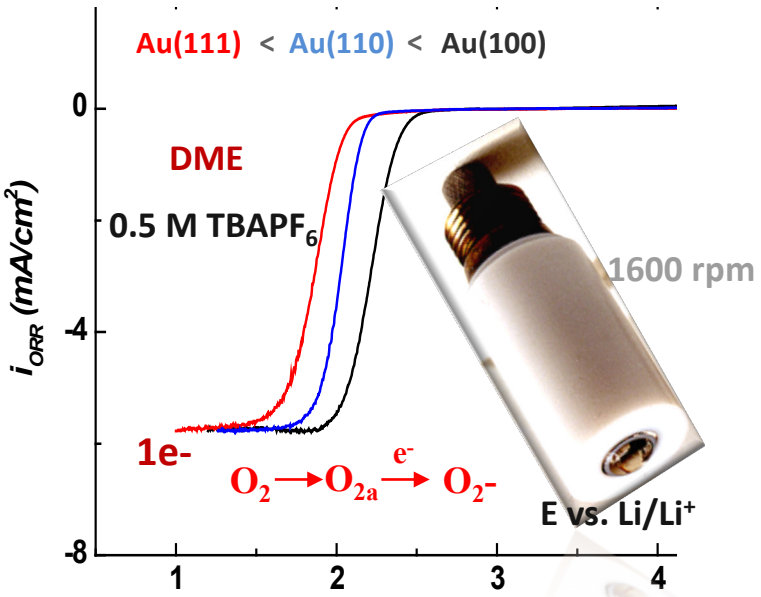
ORR/OER (electro)chemistry with Li^+

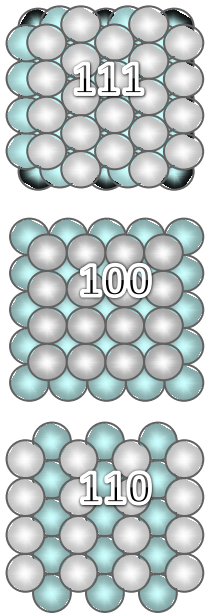
Superoxo – Lithium-Electrolyte Interactions



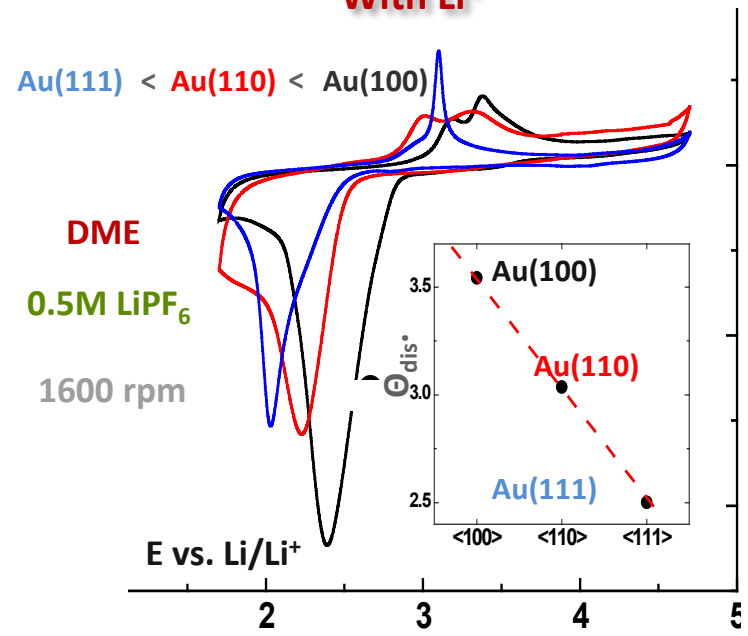
Structure sensitivity

Without Li^+



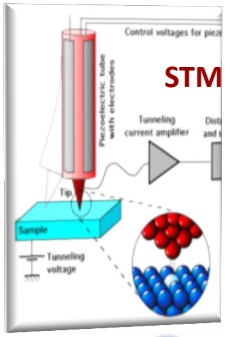


With Li^+

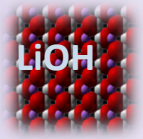


- O_2^- electrochemistry is structure sensitive
- Li-cycle is structure sensitive

ORR/OER (electro)chemistry with Li^+



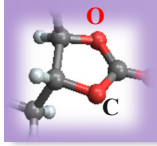
Superoxo – Lithium-Electrolyte Interactions

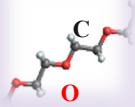


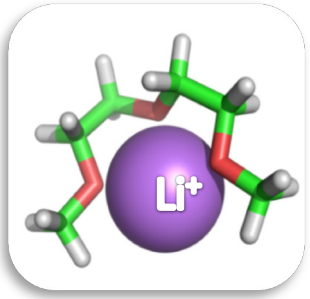
$$O_2 \leftrightarrow O_{2a} \xrightarrow[Li^+]{e^-} LiO_{2(ad)} \xrightarrow[Li^+]{e^-} Li_2O_{2(ad)}$$

$$LiO_{2(ad)} \xrightarrow{\text{disproportionation}} LiO_{2(sol)}$$

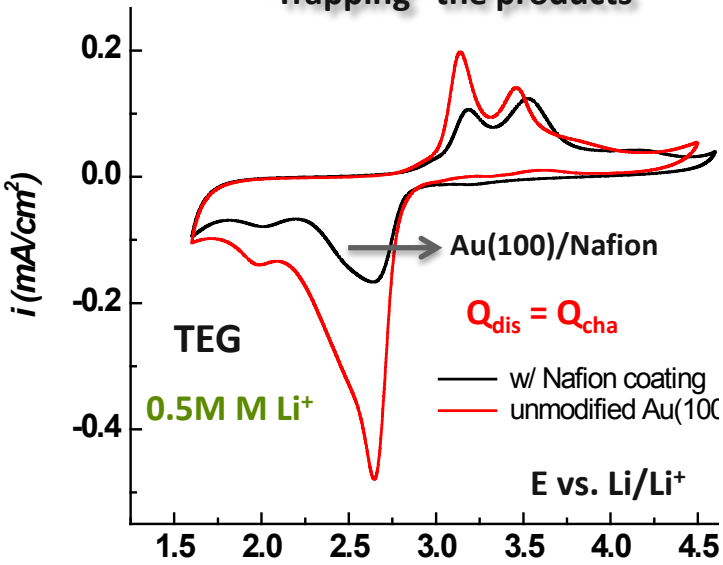
$$Li_2O_{2(ad)} \xrightarrow{\text{disproportionation}} LiO_{2(sol)}$$

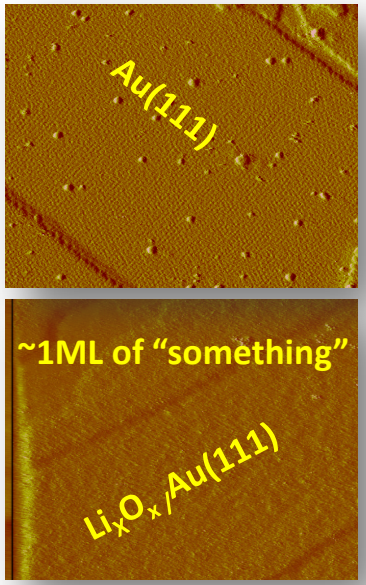




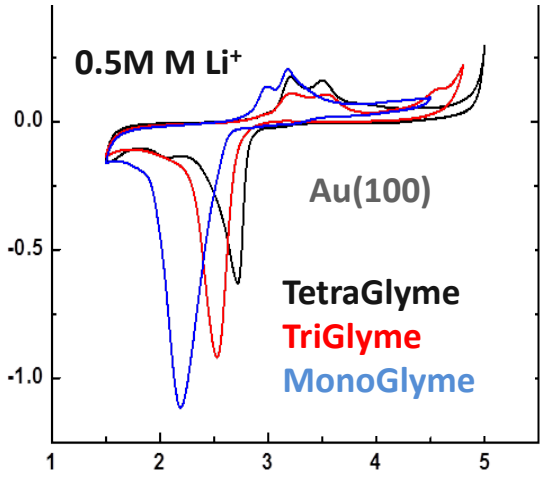


"Trapping" the products





Effect of electrolyte



- LiO_2; Li_2O_2; LiOH ; Li-???????
- Mass transport is important

Discharge:

Activity trends: TEG>TG>DME

Solvation trend : TEG<TG<DME

Charge:

Activity trends : TEG<TG<DME

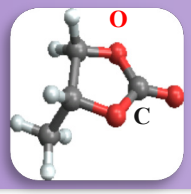
Stability trends??: TEG>TG>DME

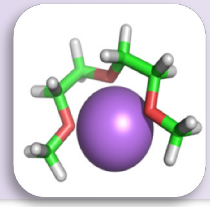
ORR/OER (electro)chemistry with KO_2

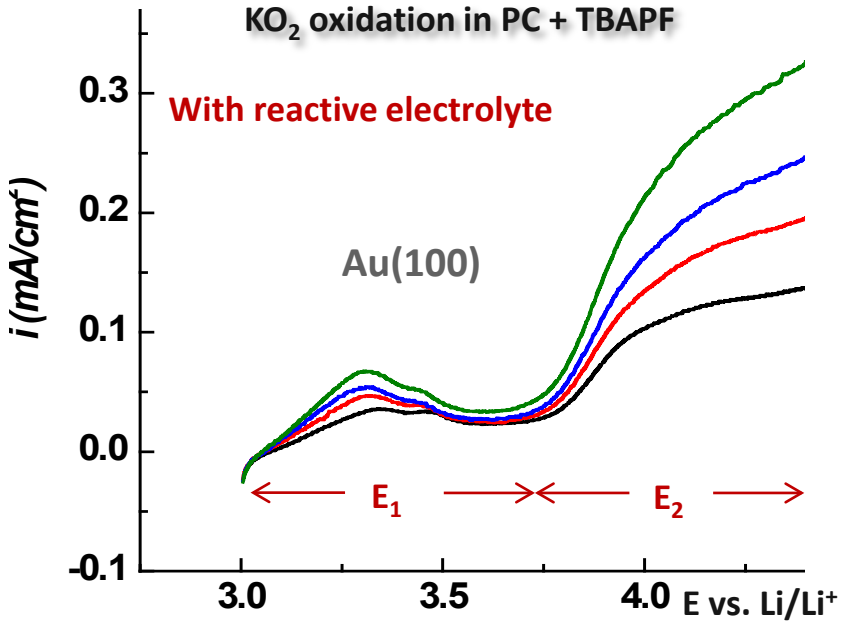
Superoxo – K(Li)-Electrolyte Interaction

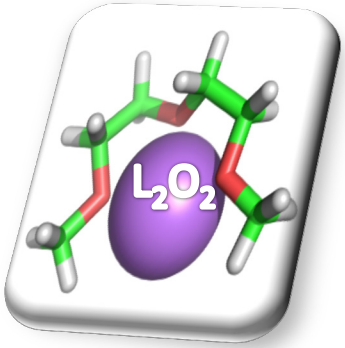
$$O_2 \longleftrightarrow O_{2(ad)} \overset{e^-}{\underset{Li^+}{\rightleftarrows}} K(Li)O_{2(ad)} \longleftrightarrow K(Li)O_{2(sol)}$$

- Faste 1st electron transfer; 2nd ????
- Weak LiO_2 /substrate interaction
- $Q_{dis.} >> Q_{cha.}$?

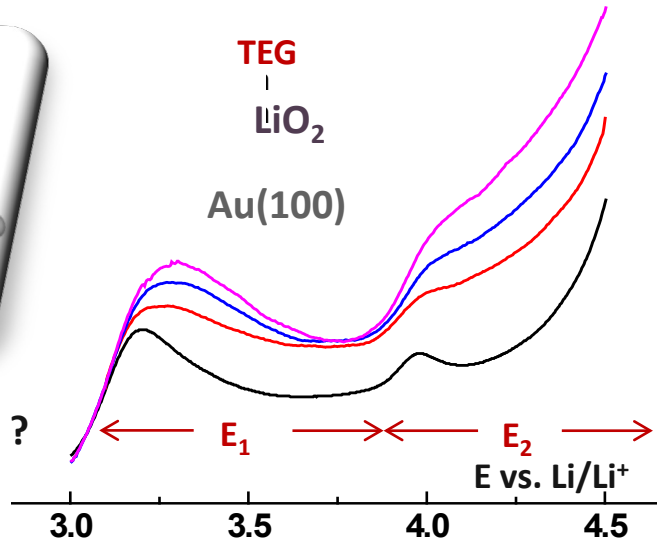








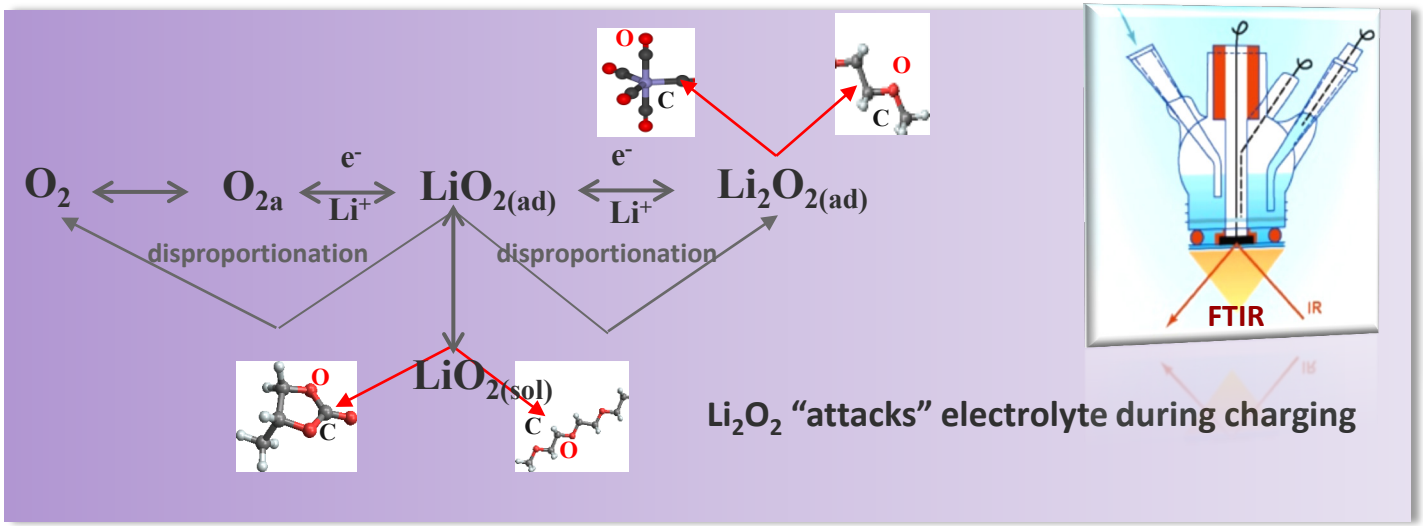
What about Li_2O_2 ?

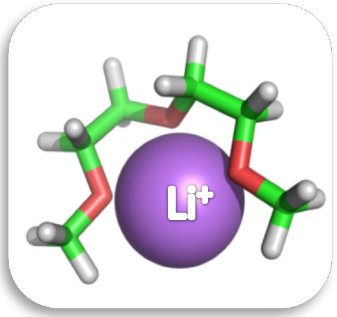


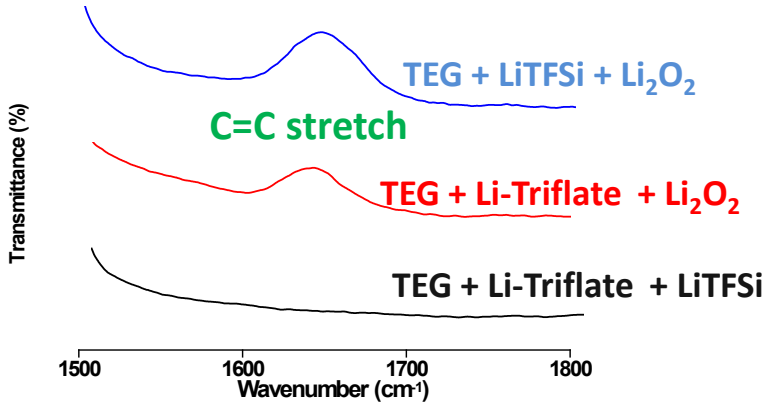
E_1: mainly KO_2 (LiO_2)oxidation

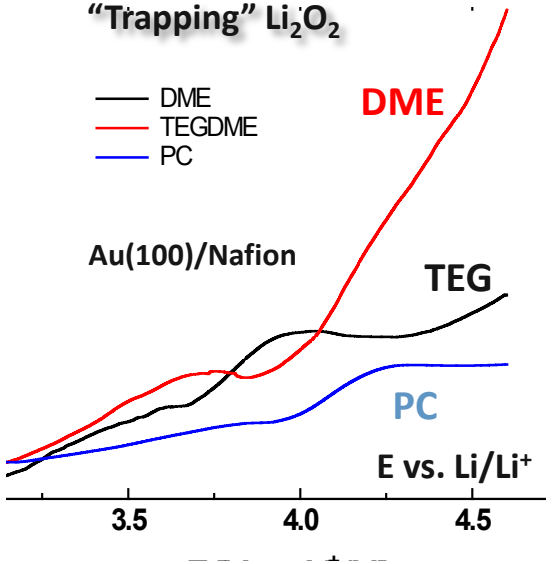
E_2: predominantly decomposition of electrolyte

ORR/OER (electro)chemistry with Li_2O_2





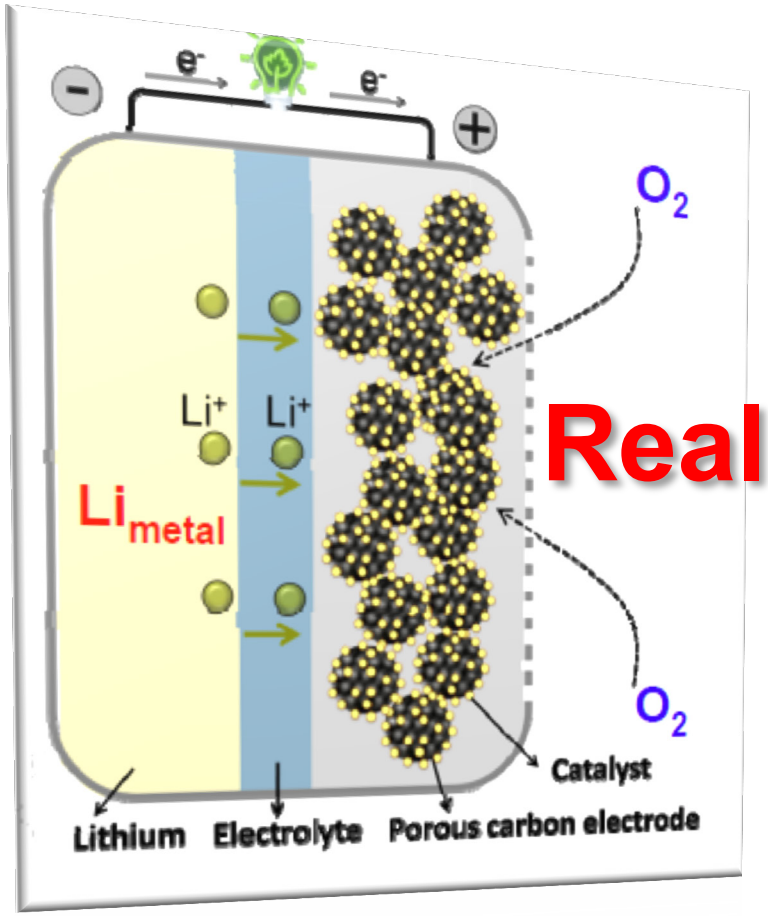




- Li_2O_2 "attacks" electrolyte above 3.5V
  - Li_2O_2 is oxidized (significantly) at and above 4,.4 V

Tailoring the future of electromobility

➢Li-air system: Combined problems of fuel cells, electrolyzers and batteries



Reality

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Chao Wang

Voya Stamenkovic

DOE – BES: FWP and EFRC

➢Fascinating scientific questions (and technological opportunities ????)