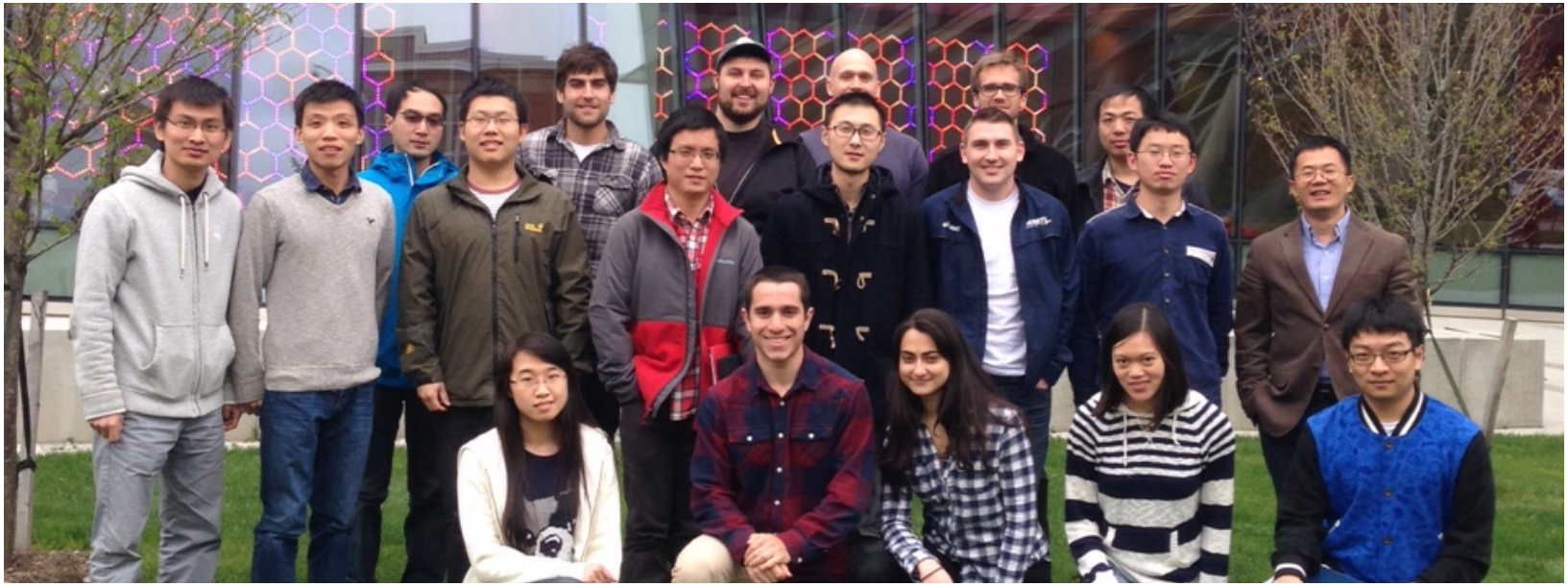
Rechargeable K-O_2 batteries: principle, mechanism & challenge

Yiying Wu （吴屹影）

Professor
Department of Chemistry & Biochemistry
The Ohio State University
Columbus, Ohio

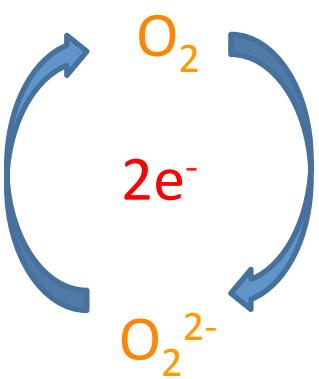


Challenge in oxygen reduction/evolution

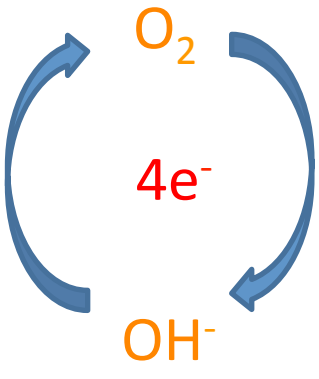
Metal-air batteries

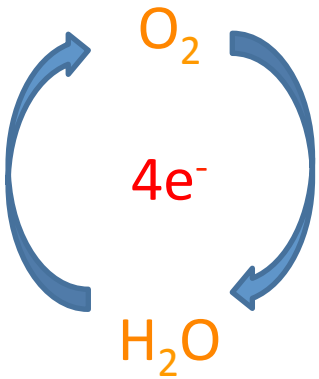
Fuel cell/
water splitting

Li-air



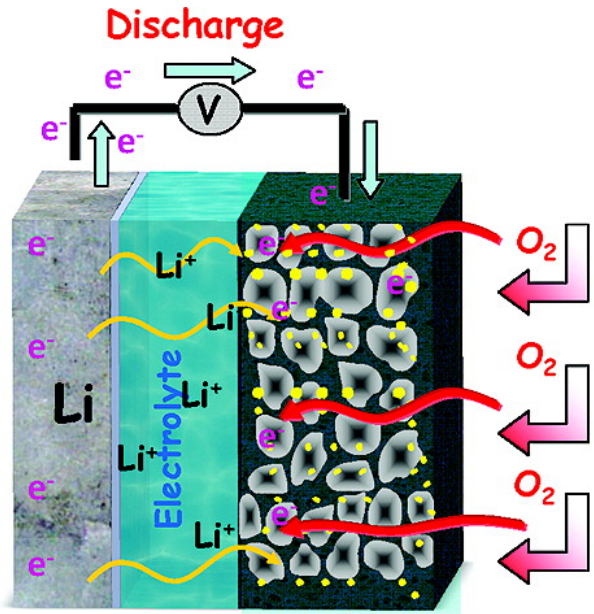
Zn-air

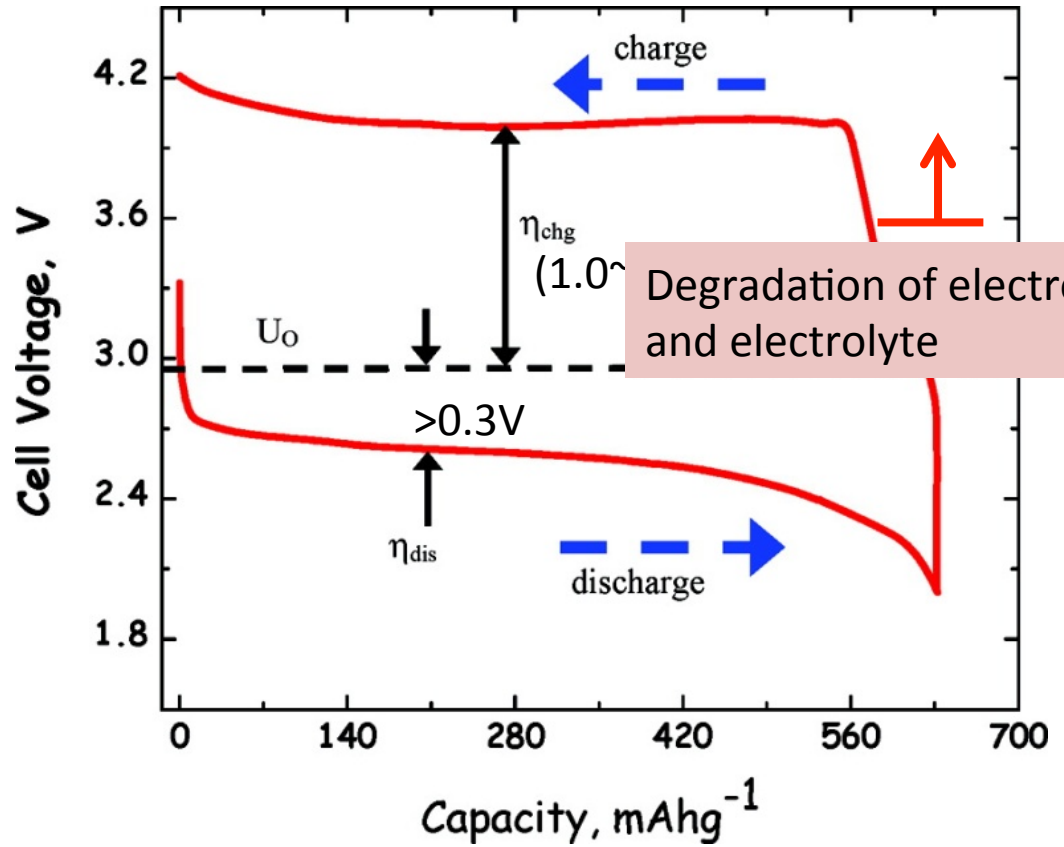




- **Multi-electron transfer**
- **High cost catalysts**

Li-O_2 Battery





$$2Li + O_2 = Li_2O_2$$

Large charging overpotential and the resultant electrode/ electrolyte decomposition is a grand challenge in Li-O_2 batteries

Ottakam Thotiyl, M. M. et al. *J. Am. Chem. Soc.135*, 494–500 (2013)

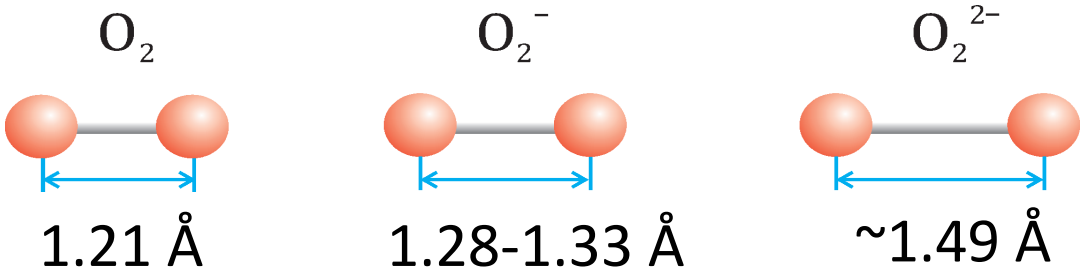
An idea from General Chemistry

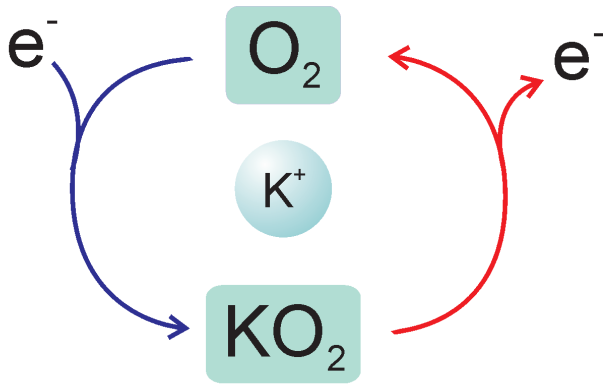
Pop quiz

$Li + O_2 \rightarrow Li_2O$

$Na + O_2 \rightarrow Na_2O_2$

$K + O_2 \rightarrow KO_2$



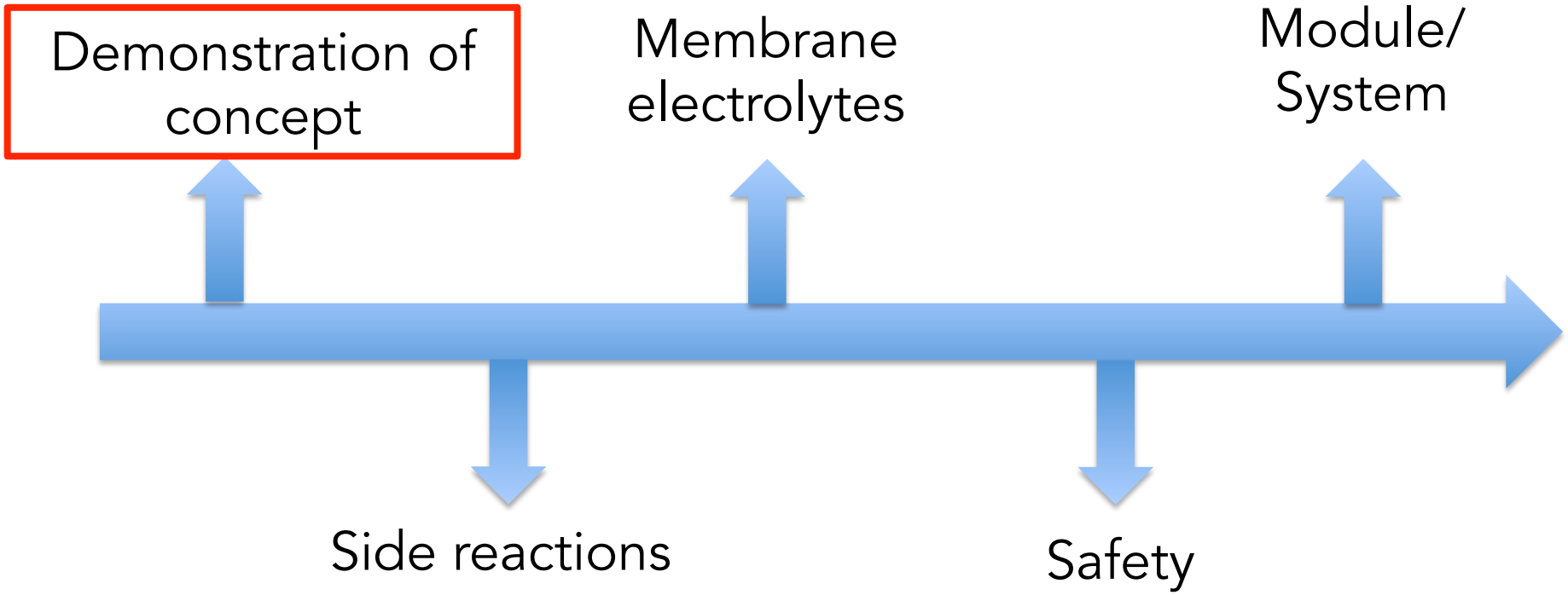


$$K + O_2 \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} KO_2$$

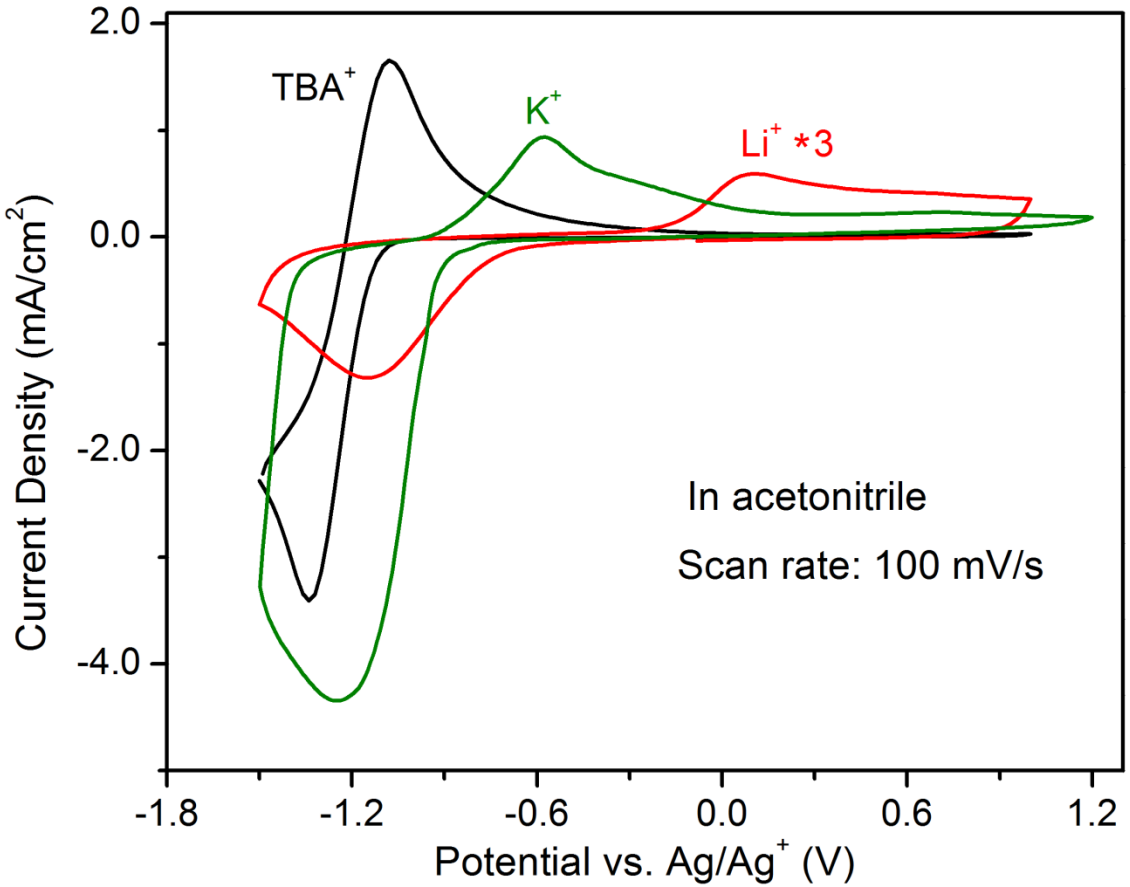
ΔG^o=-239.4 kJ/mol

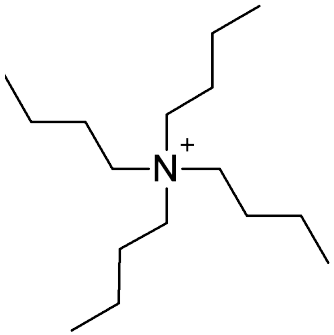
Specific Energy= 934.9 Wh/kg (based on KO_2)

Development Map of K-O_2 Battery

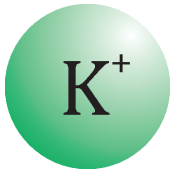


The Influence of Cations on O_2 Redox Chemistry





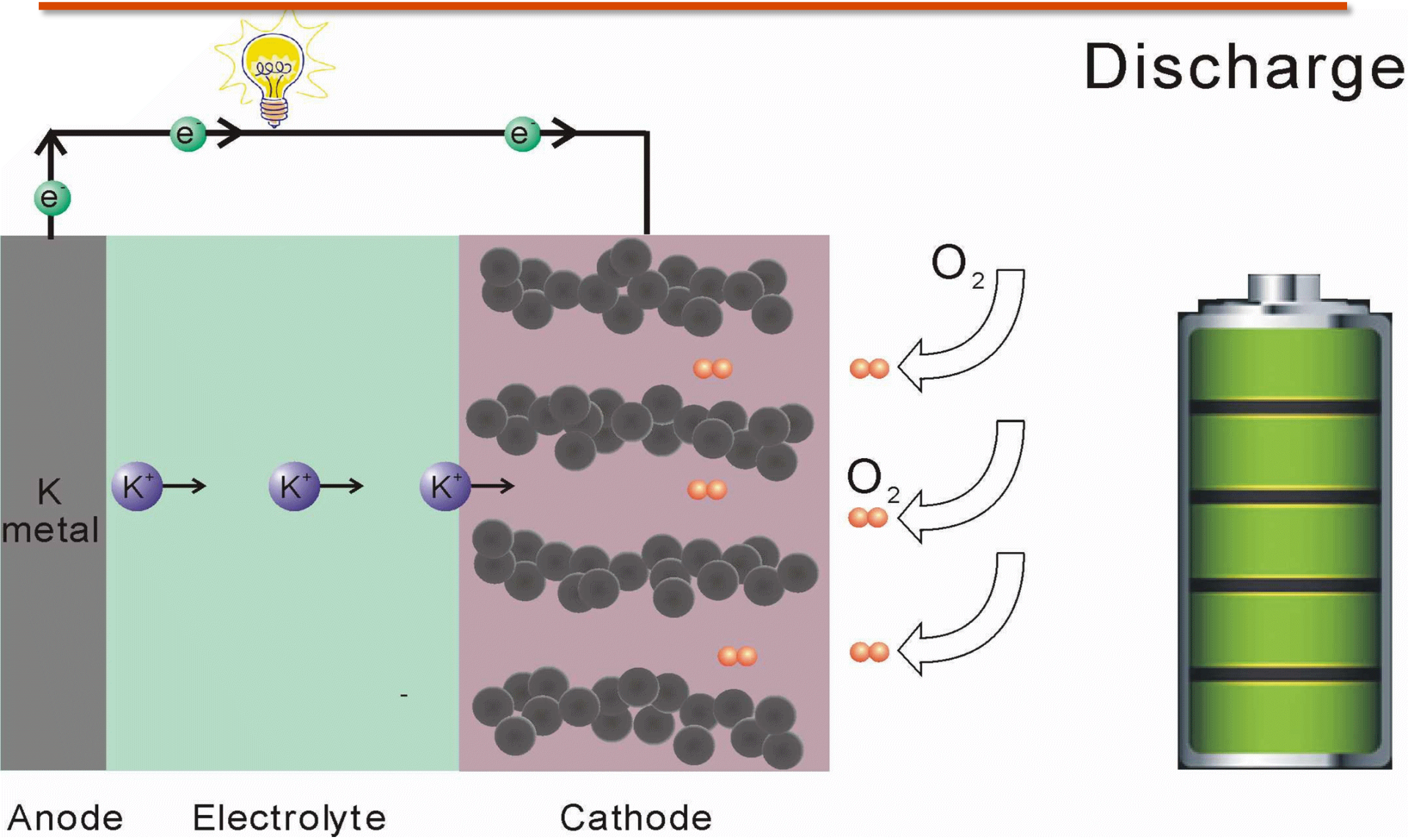
TBA$^+$



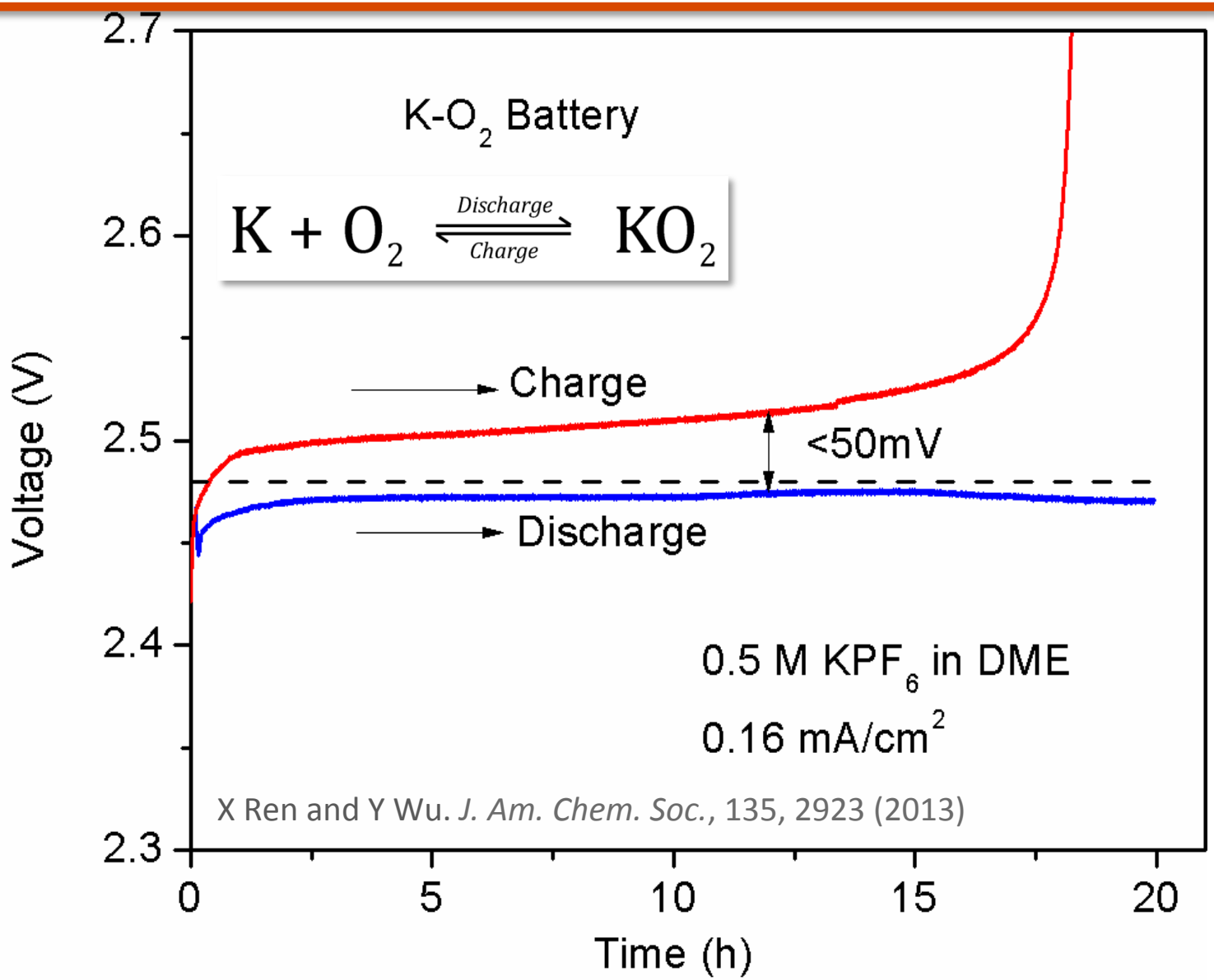
"Soft" cation stabilizes superoxide ions and increases reversibility

X Ren and Y Wu. *J. Am. Chem. Soc.*, 135, 2923 (2013)

K-O_2 battery: how it works



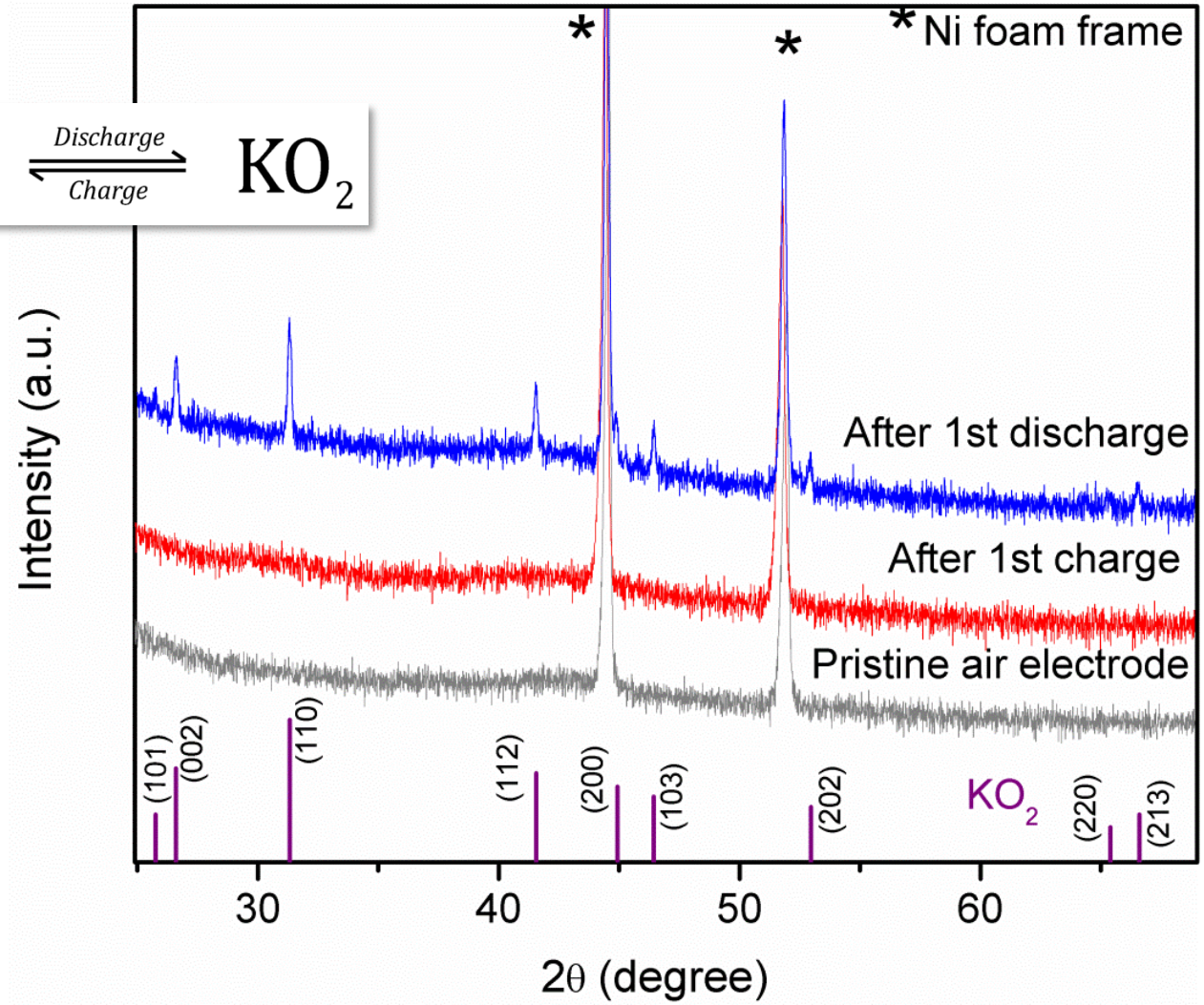
Battery Test



X Ren and Y Wu. *J. Am. Chem. Soc.*, 135, 2923 (2013)

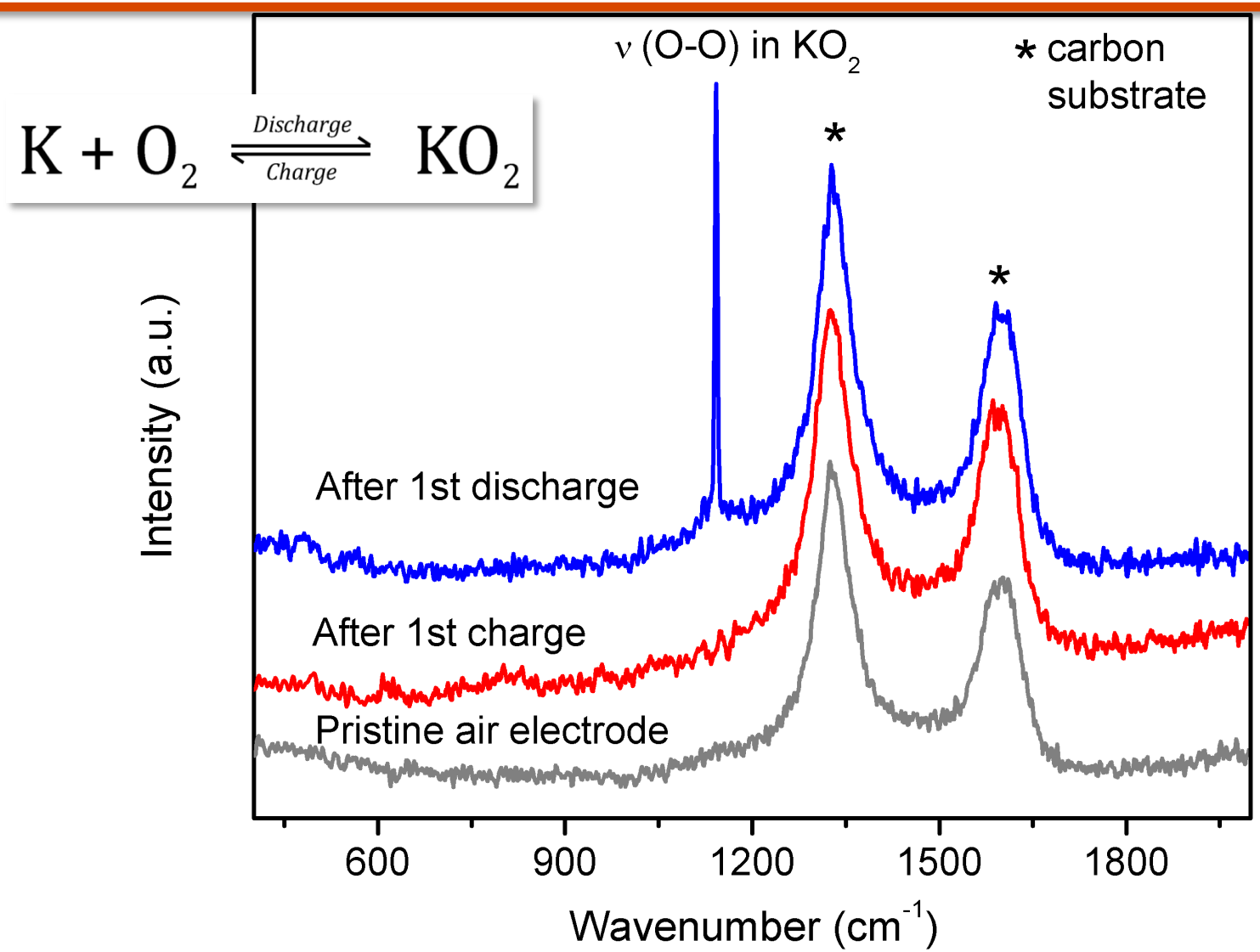
X-ray diffraction

$$K + O_2 \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} KO_2$$



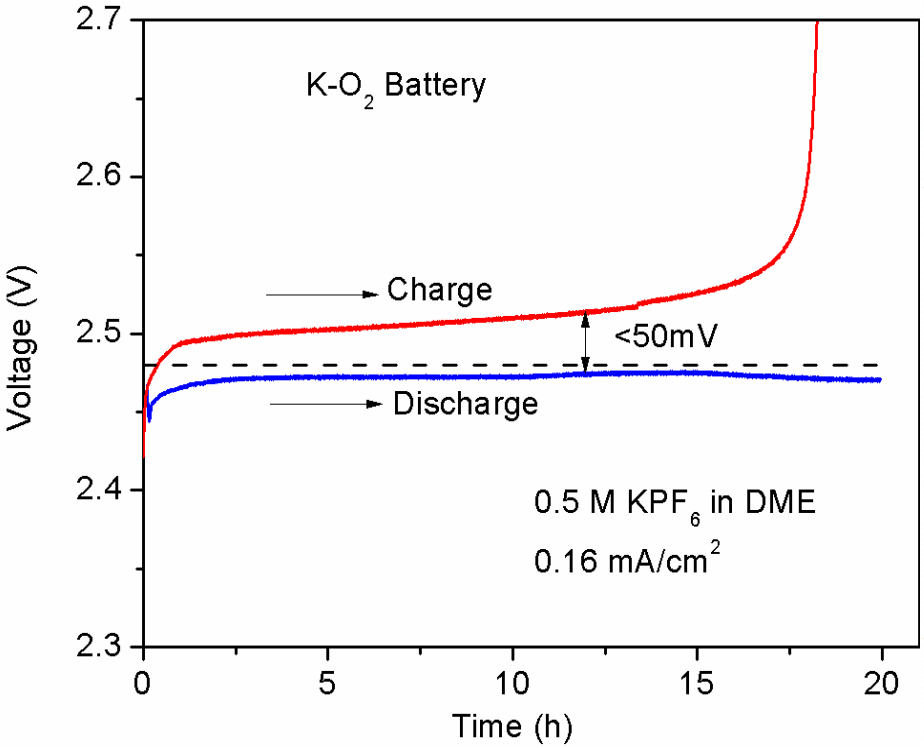
X Ren and Y Wu. *J. Am. Chem. Soc.*, 135, 2923 (2013)

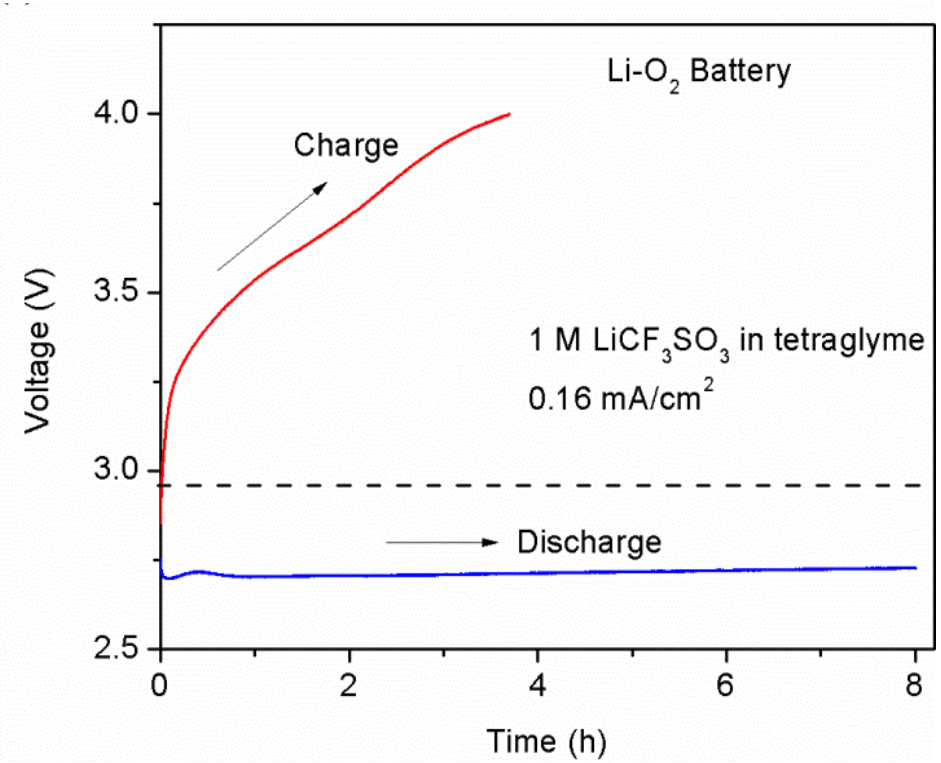
Raman Characterization



X Ren and Y Wu. *J. Am. Chem. Soc.*, 135, 2923 (2013)

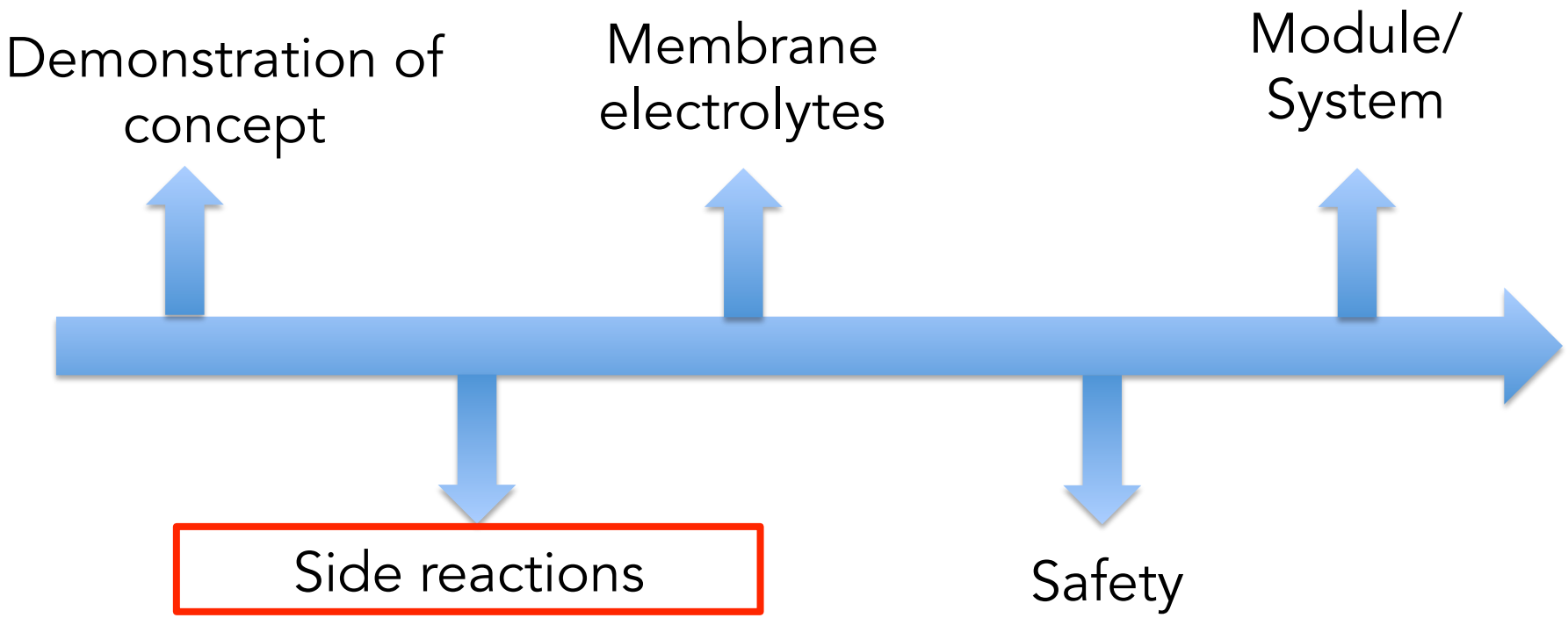
$K\text{-}O_2$ vs. $Li\text{-}O_2$



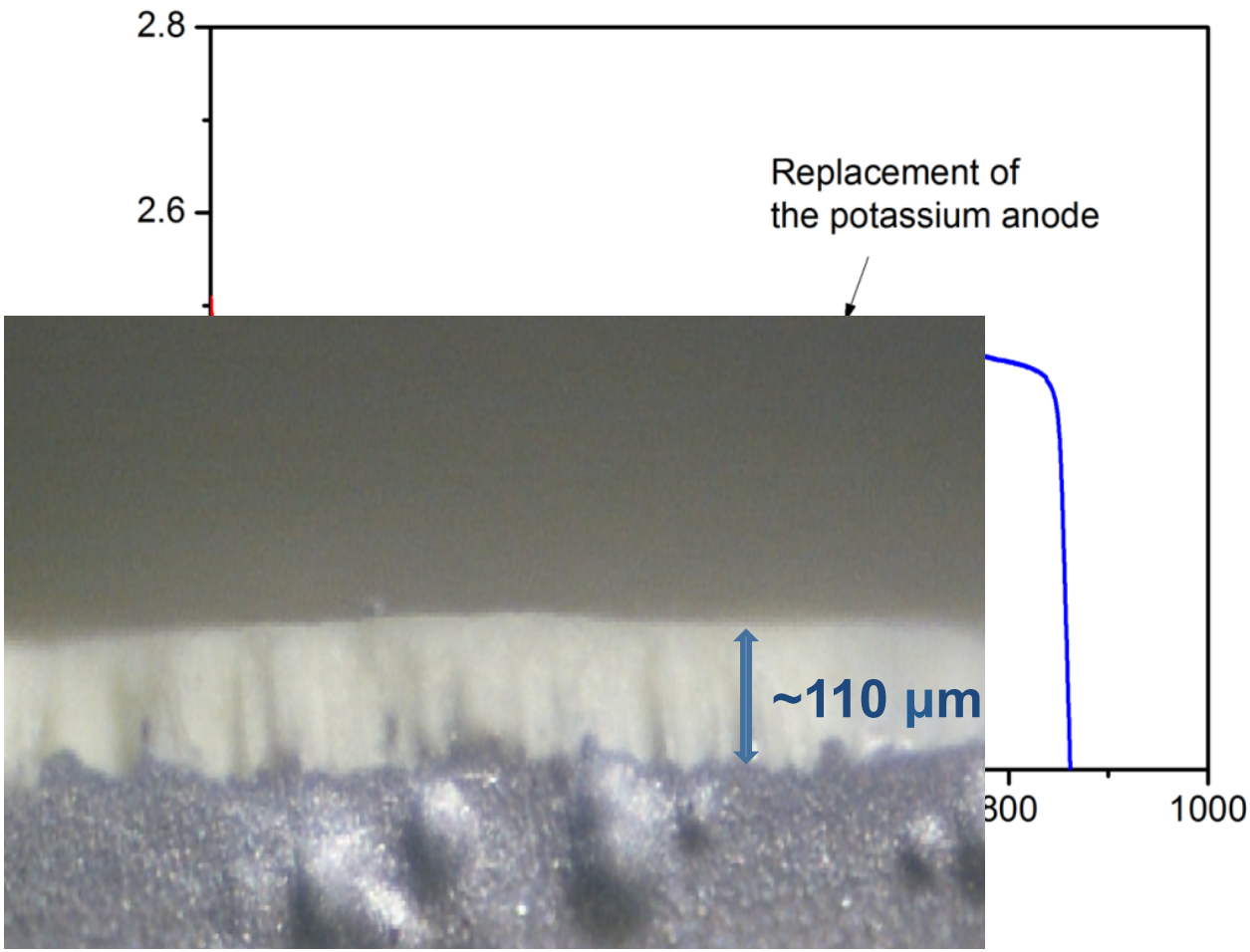


PCT patent filed (Application No. PCT/US14/12730)

Development Map of K-O_2 Battery



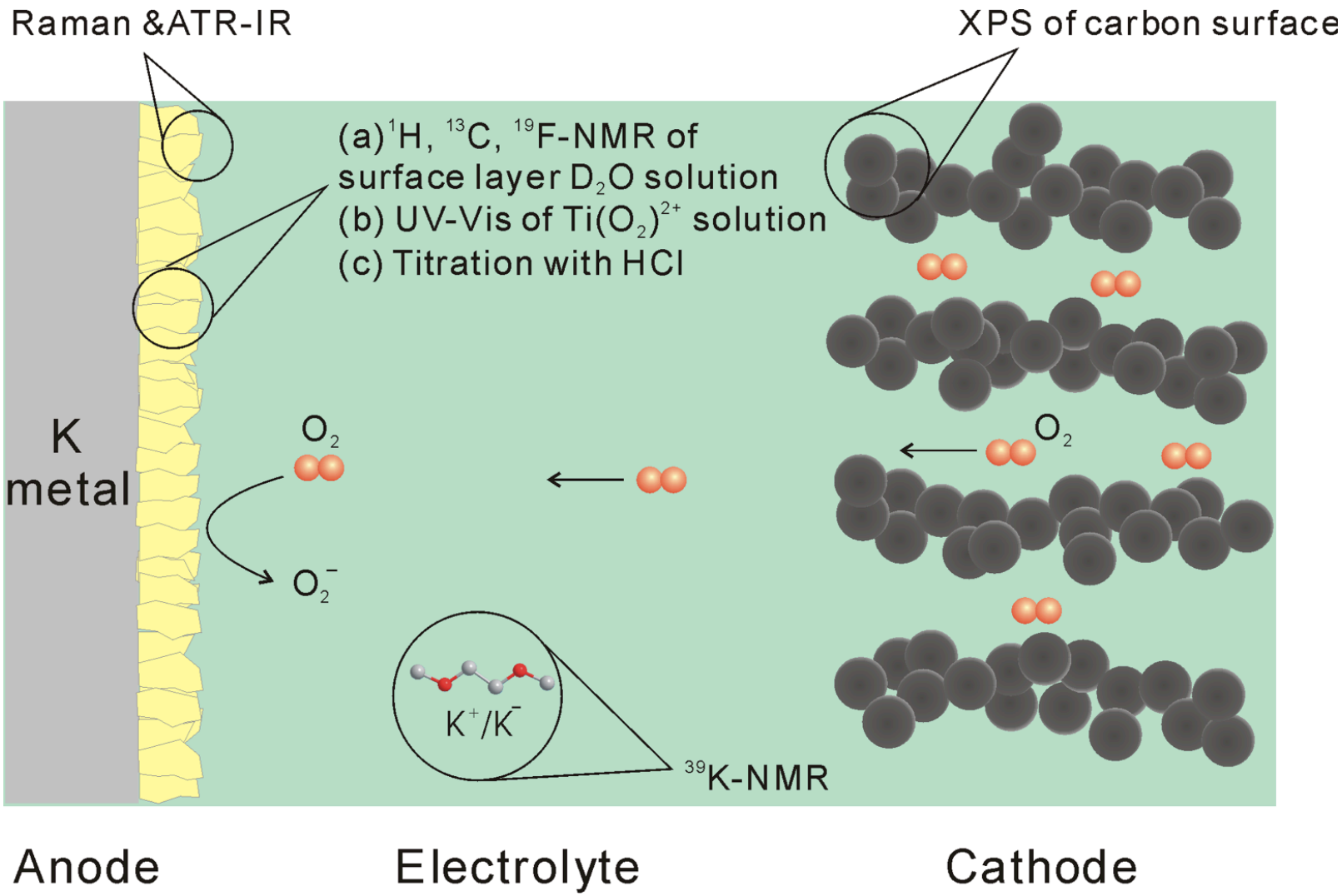
Which electrode limits the performance: metal or oxygen electrode?



The growth of a surface layer on the K anode

- Xiaodi Ren etc, *ACS Applied Materials and Interfaces*, 2014.

Examining Side Products



Species in the surface layer

Table 1. Compositions in the surface layers after battery cycle and discharge tests

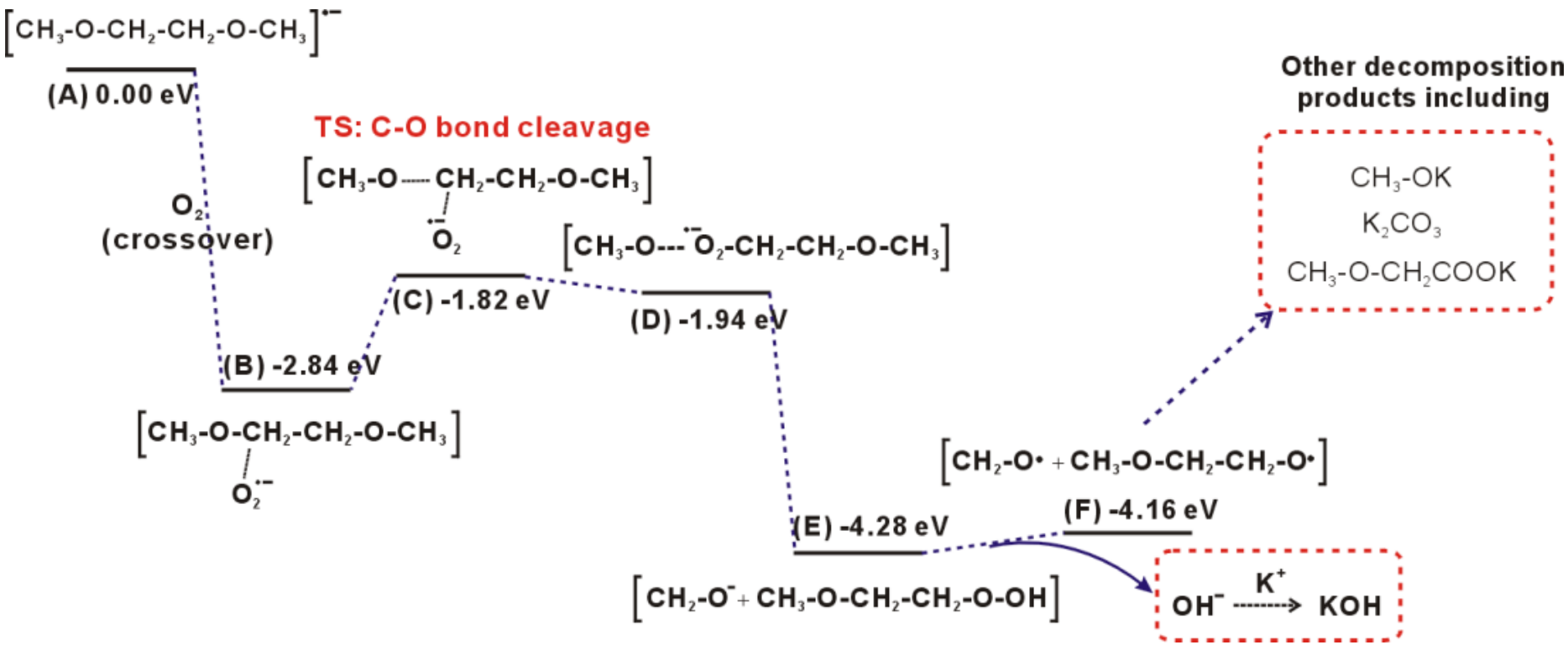
Components (wt)%	After cycle tests			After discharge tests	
	Sample A	Sample B	Sample C	Sample D	Sample E
KO_2	22.2%	20.5%	22.1%	27.2%	26.1%
KPF_6	10.7 %	9.7 %	12.9 %	13.4 %	15.4 %
KOH	44.3 %	48.0 %	42.9 %	41.2 %	39.5 %
K_2CO_3	5.2 %	6.0 %	8.0 %	5.9 %	6.3 %
Organic side products	2.6 %	2.7 %	3.9%	4.3 %	5.0 %
Sum	85.0 %	86.9 %	89.8 %	92.0 %	92.3 %

Similar composition ratios in the anode surface layer whether after discharge or cycle tests

Similar Raman spectrum on K electrode even without tests

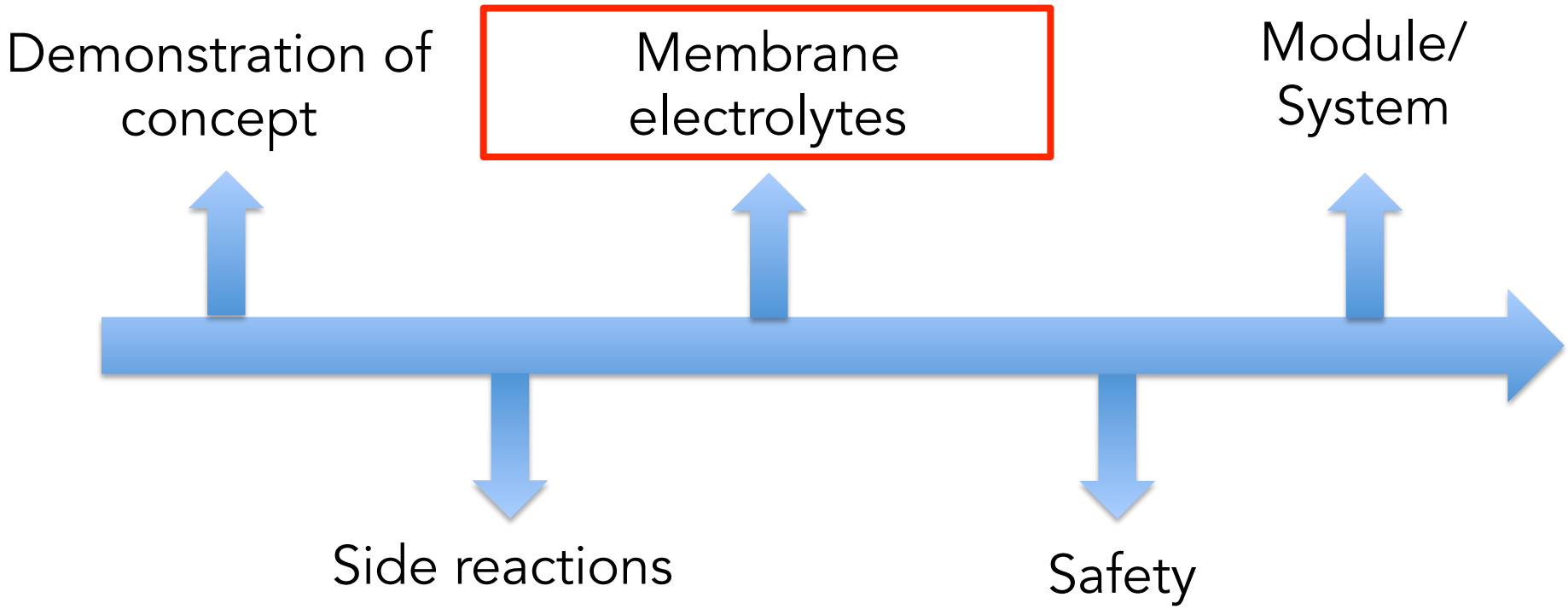
The growth of the surface layer: the direct reaction between K and electrolyte

Proposed mechanism of electrolyte decomposition

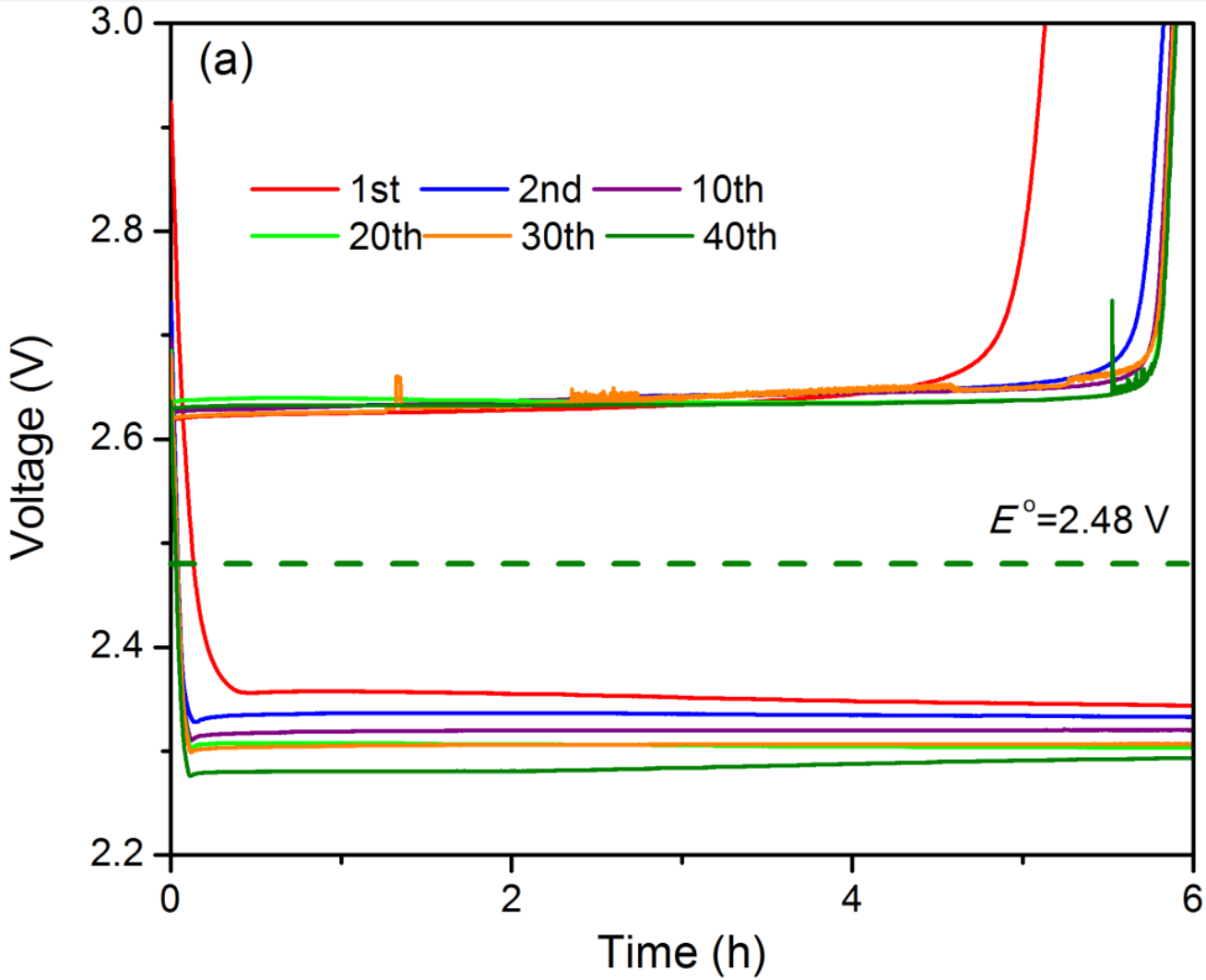


By Kah Chun Lau, Larry Curtiss at ANL

Development Map of K-O_2 Battery

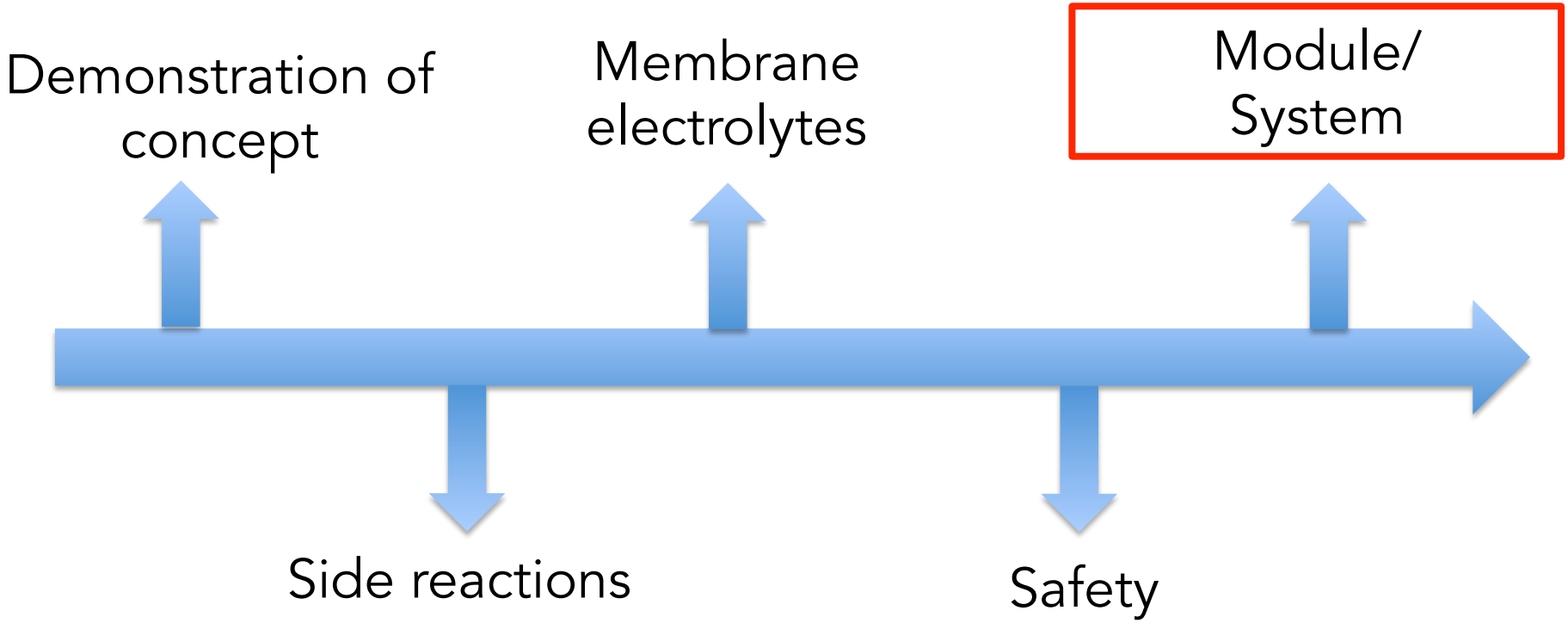


K^+-Nafion membrane for improving cycle life

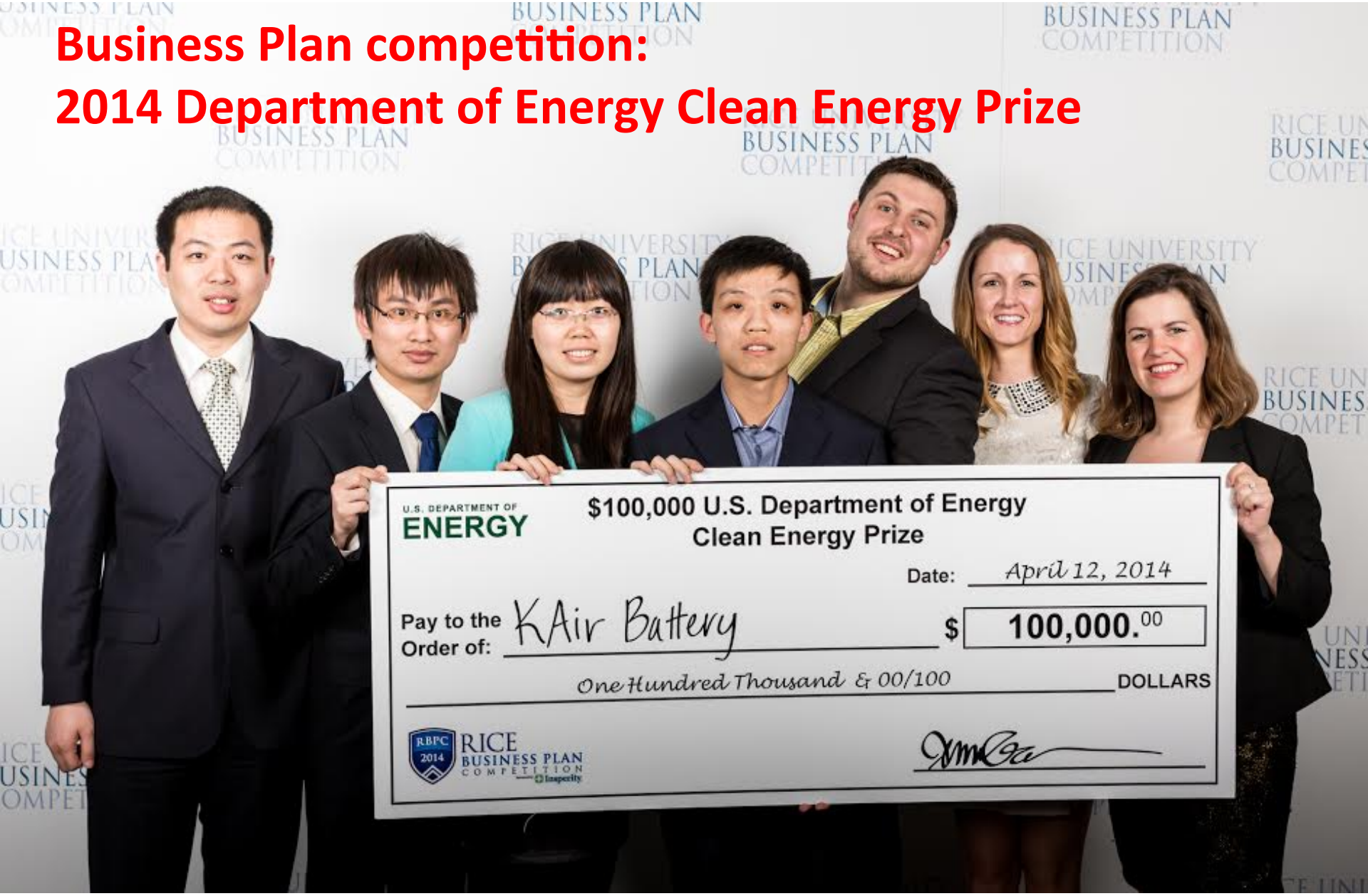


X. Ren, et al, *ACS Appl. Mater. Interfaces* 2014, 6, 19299−19307
X. Bi, et al, *Chem.Commun.*, 2015, 51, 7665—7668

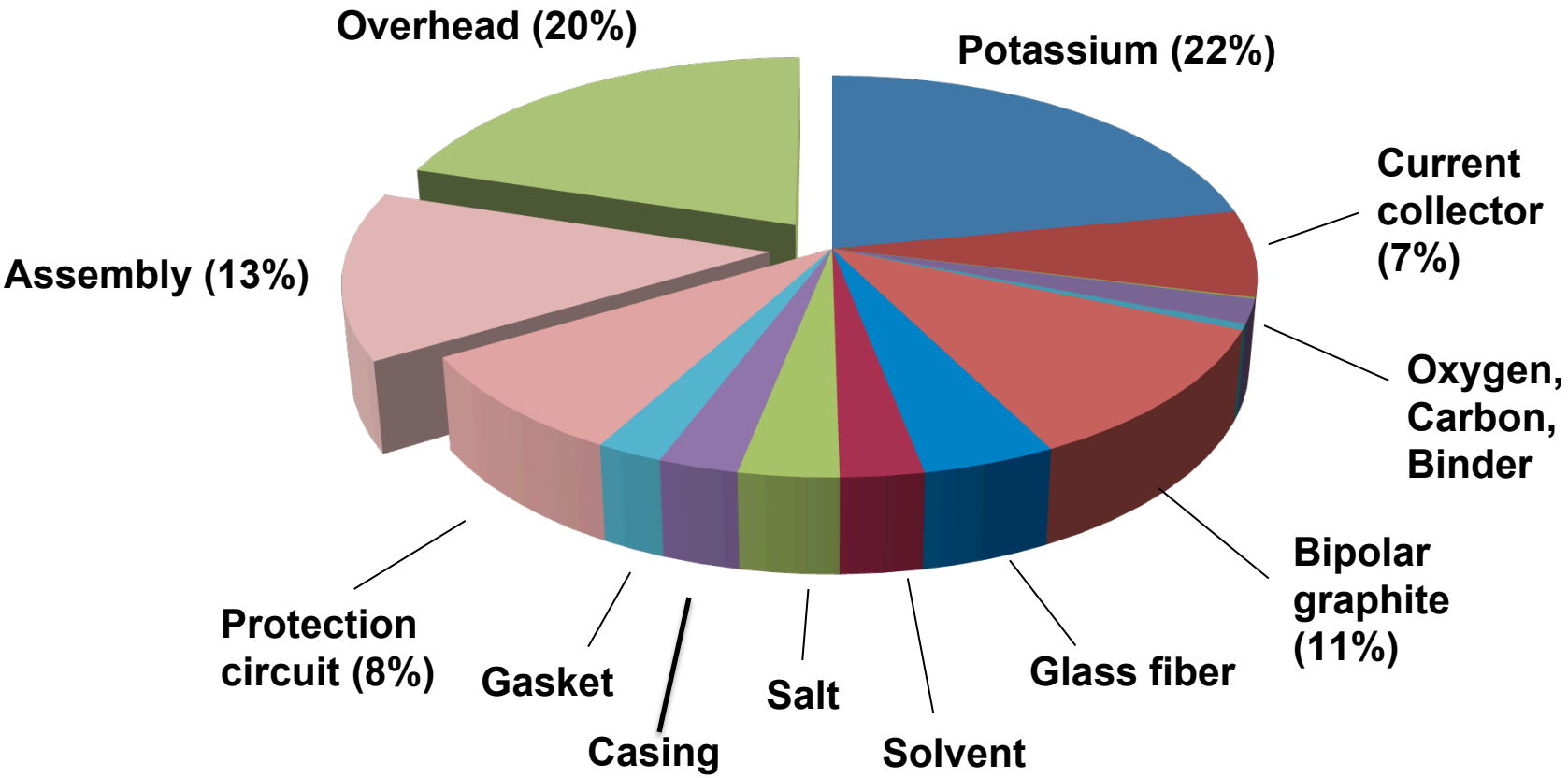
Development Map of K-O_2 Battery



Business Plan competition:
2014 Department of Energy Clean Energy Prize



Production Cost = $89 / kWh



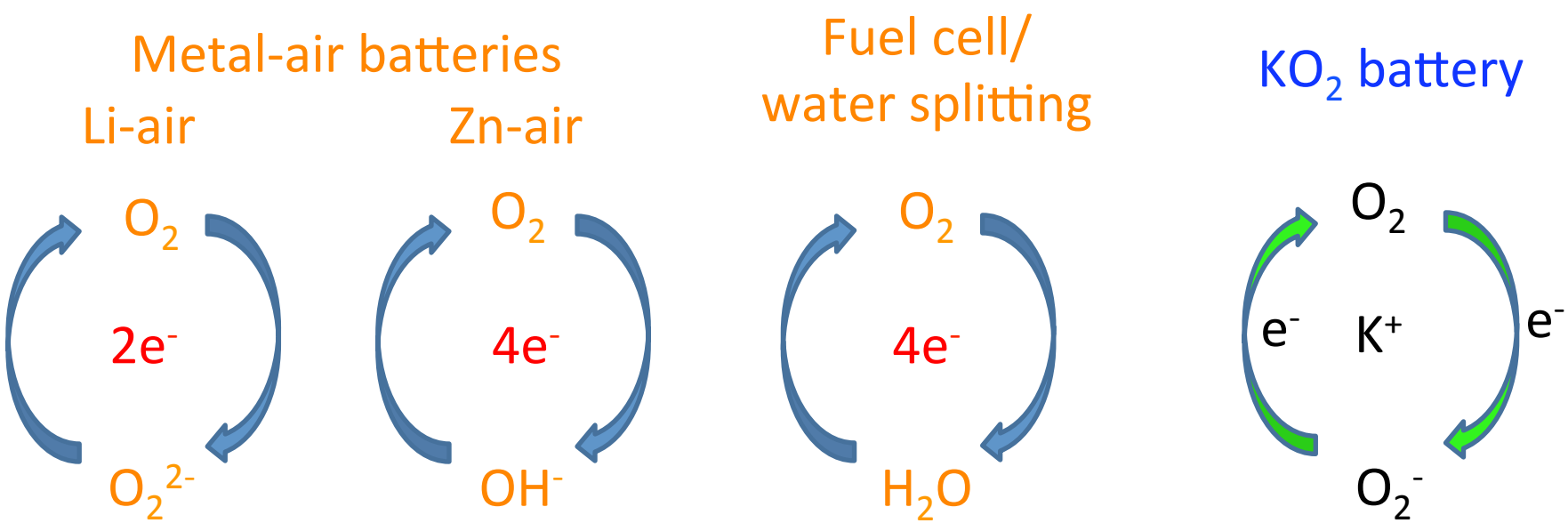
Cost of competing products = $300 to $1300

Summary

1: K-O_2 battery is based on a reversible single-electron redox between O_2 and KO_2, eliminating the need of ORR/OER electrocatalysts;

2: Easy scale-up, low cost and high energy density are advantages.

3: Safety can be addressed through alternative anodes and membrane protection.



High cost catalysts
Multiple electron transfers

No need for catalysts
Single electron

Current group members

Zhongjie Huang, Mingzhe Yu, Thomas Draskovic, Mingfu He, Lu Ma, Xiaodi Ren, Kevin Click, Damian Beauchamp, Xuanxuan Bi, Ben Garrett , Billy McCulloch, Yongze Yu, Neng Xiao

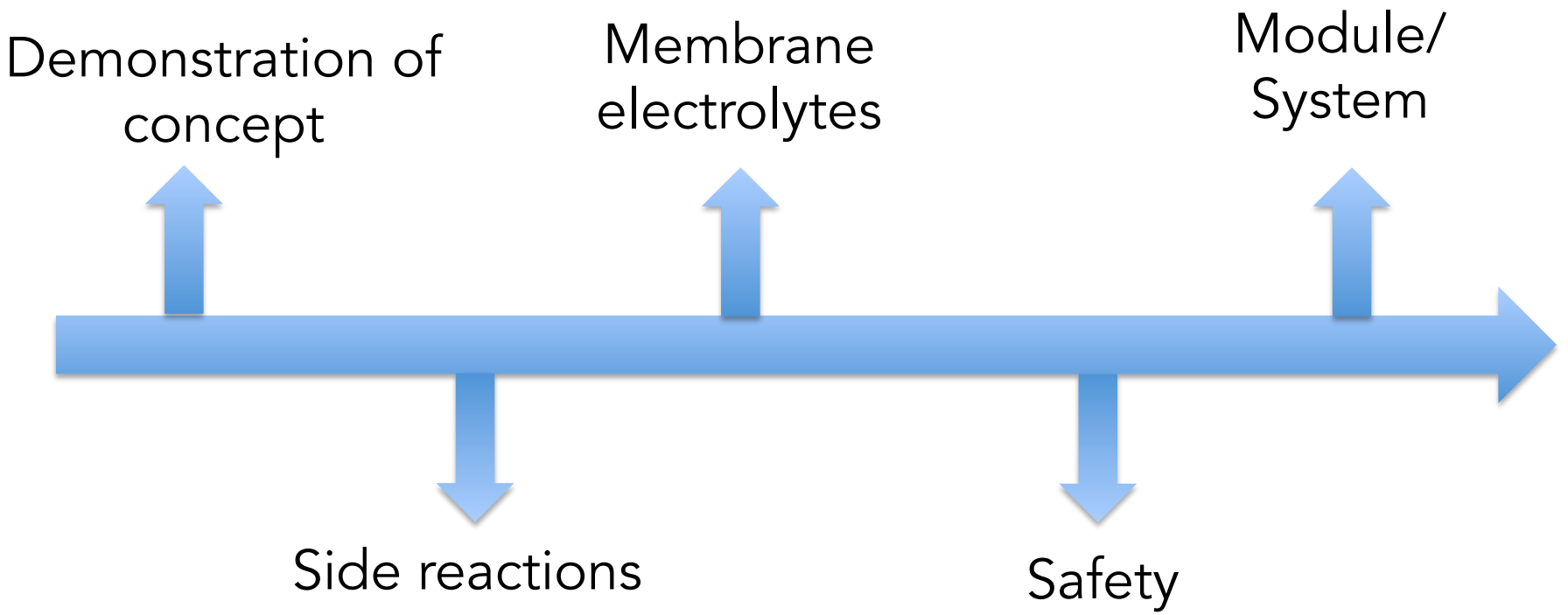
Alumni

Zhiqiang Ji (Los Alamos NL), Gayatri Natu (India)
Panitat Hasin (Kasetsart Univ), Yanguang Li (Soochow Univ), Bing Tan (IMRA), Mario Alpuche (Univ. Nevada, Reno), Dr. Weilin Chen (Northwest Normal Univ)

Collaborators

Xiaoyi Zhang, Jun Lu/Khalil Amine, Kah Chun Lau/Larry Curtiss (Argonne), Don Siegel (UMich), Vishnu Sundaresan, Umit Ozkan, Siddharth Rajan, Christopher Hadad, Claudia Turro, Aravind Asthagiri (OSU)

Funding Map of K-O_2 Battery



IMR Institute For Materials Research

NSF

HRI Honda Research Institute

Ohio Development Services Agency