

# Fundamentals & Applications of Electrochemical Capacitors

Veronica Augustyn ([vaugust@ncsu.edu](mailto:vaugust@ncsu.edu))

Assistant Professor

Dept. of Materials Science & Engineering

North Carolina State University

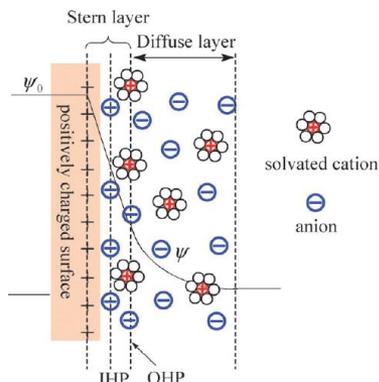
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Advances, Challenges, and Long-Term Opportunities for Electrochemistry

A Chemical Sciences Roundtable

Washington, DC, November 18, 2019

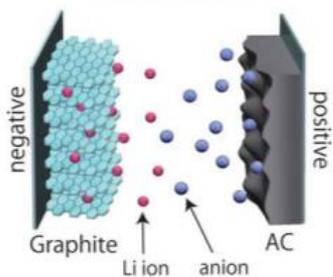
# Key Points



## Energy Storage at Electrochemical Interfaces

*Chem. Soc. Rev.* 38 (2009) 2520.

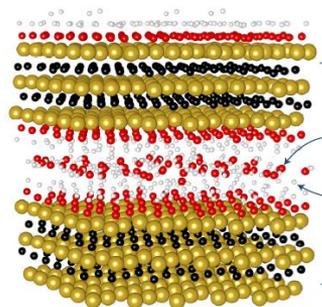
- Electrosorption & chemisorption of ions
- Excellent electrochemical reversibility
- No solid state mass transfer limitations



## Devices & Applications

*Energy & Environ. Sci.*, 5 (2012) 9363.

- High power
- High reliability
- Complementary to batteries; take advantage of batteries for hybrid devices

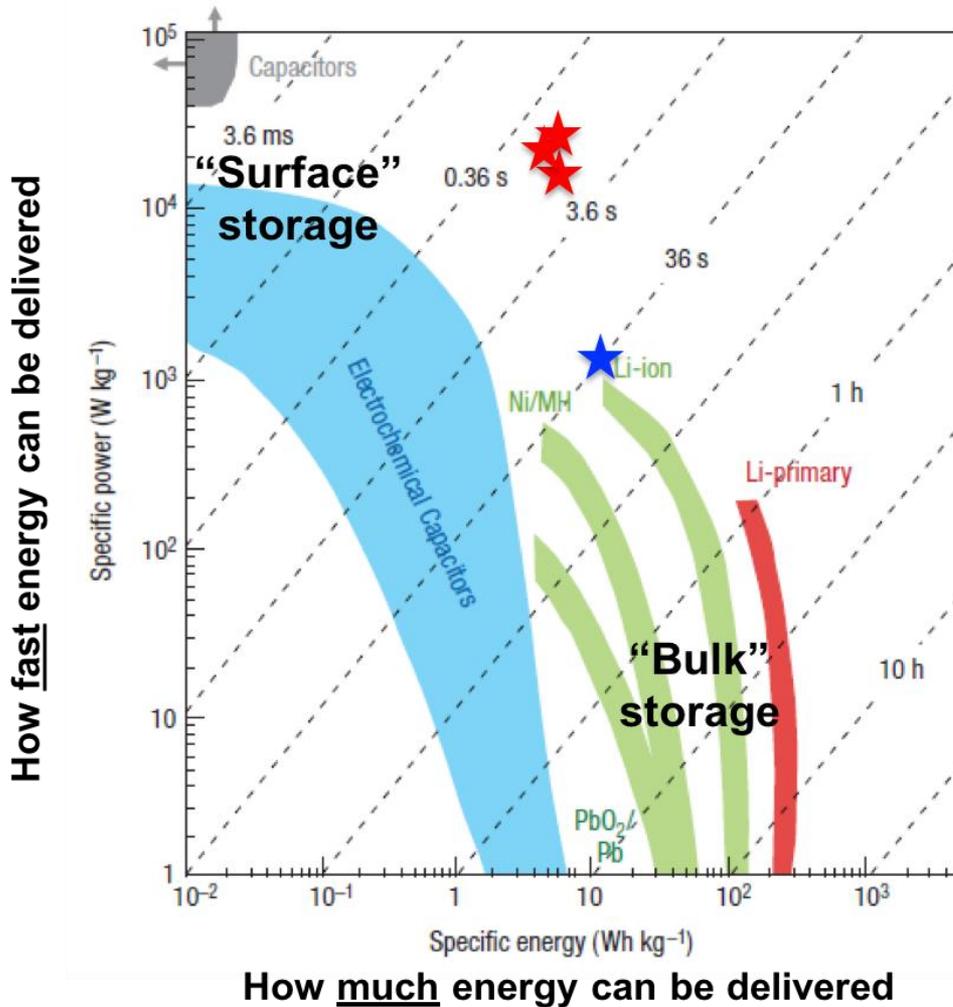


## Emerging Materials & Concepts

*Nature Energy* 2 (2017) 17105.

- New materials & advanced characterization challenge traditional views of surface storage
- Insertion/intercalation processes critical for obtaining simultaneous high energy + high power
- Understanding confinement is crucial

# What are electrochemical capacitors? (ultracapacitors, supercapacitors)



## Electric Double Layer Capacitor

Capacitance: 3200 F  
 Voltage: 2.85 V  
 Specific Energy: 6.82 Wh/kg  
 Specific Power: 32 kW/kg  
 Cycles: 1,000,000  
 Weight: 530 g  
 Source: Skeleton SCA 3200



## Hybrid Li-ion Capacitor

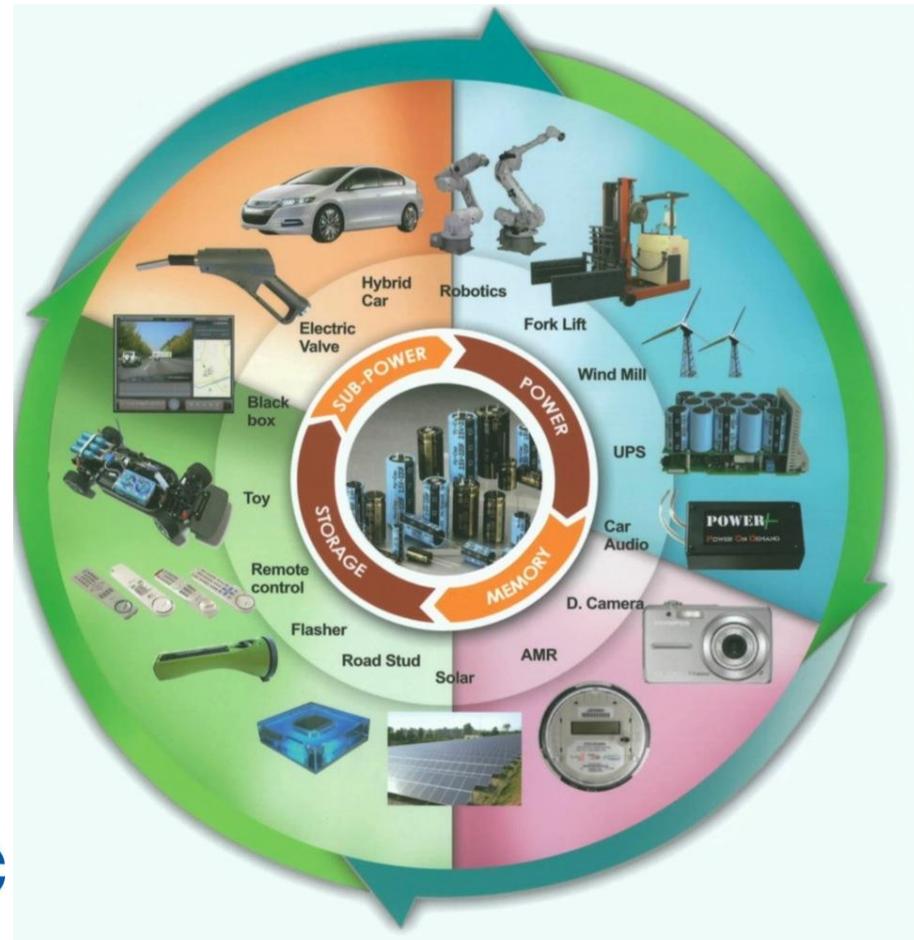
Capacitance: 3300 F  
 Voltage: 2.2 - 3.8 V  
 Specific Energy: 13 Wh/kg  
 Specific Power: 11 kW/kg  
 Cycles: 600,000  
 Weight: 350 g  
 Source: JM Energy 3300F Prismatic

# Electrochemical Capacitor Applications

Electrochemical capacitors offer:

- high power densities  
→ deliver & accept large currents, quickly
- excellent kinetics  
→ high energy efficiency at high power
- intermediate energy densities  
→ store energy and power devices
- reliability  
→ long lifetime, > 500,000 cycles

Examples of Manufacturers:



Source: Hy-Cap/VinaTech

Market Size: ~ \$1 billion (LIBs: ~ \$40 billion)

# 1954: 1st Patent for Electric Double Layer Capacitors (EDLCs) Granted to GE

July 23, 1957

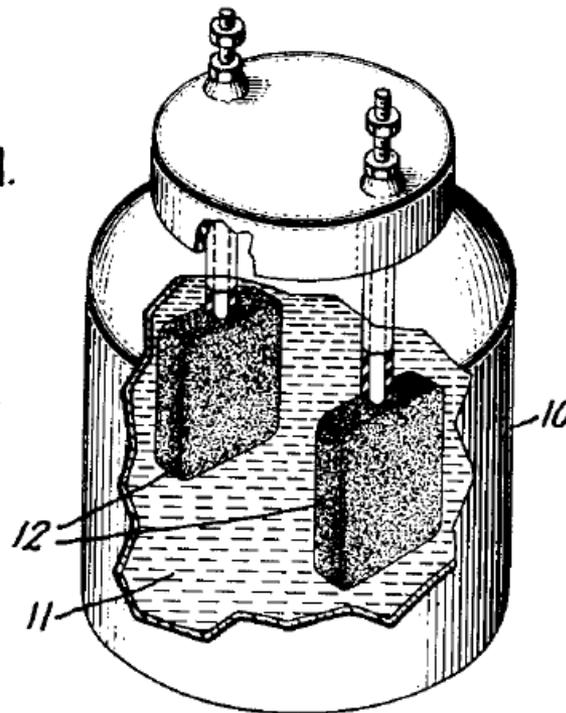
H. I. BECKER

2,800,616

LOW VOLTAGE ELECTROLYTIC CAPACITOR

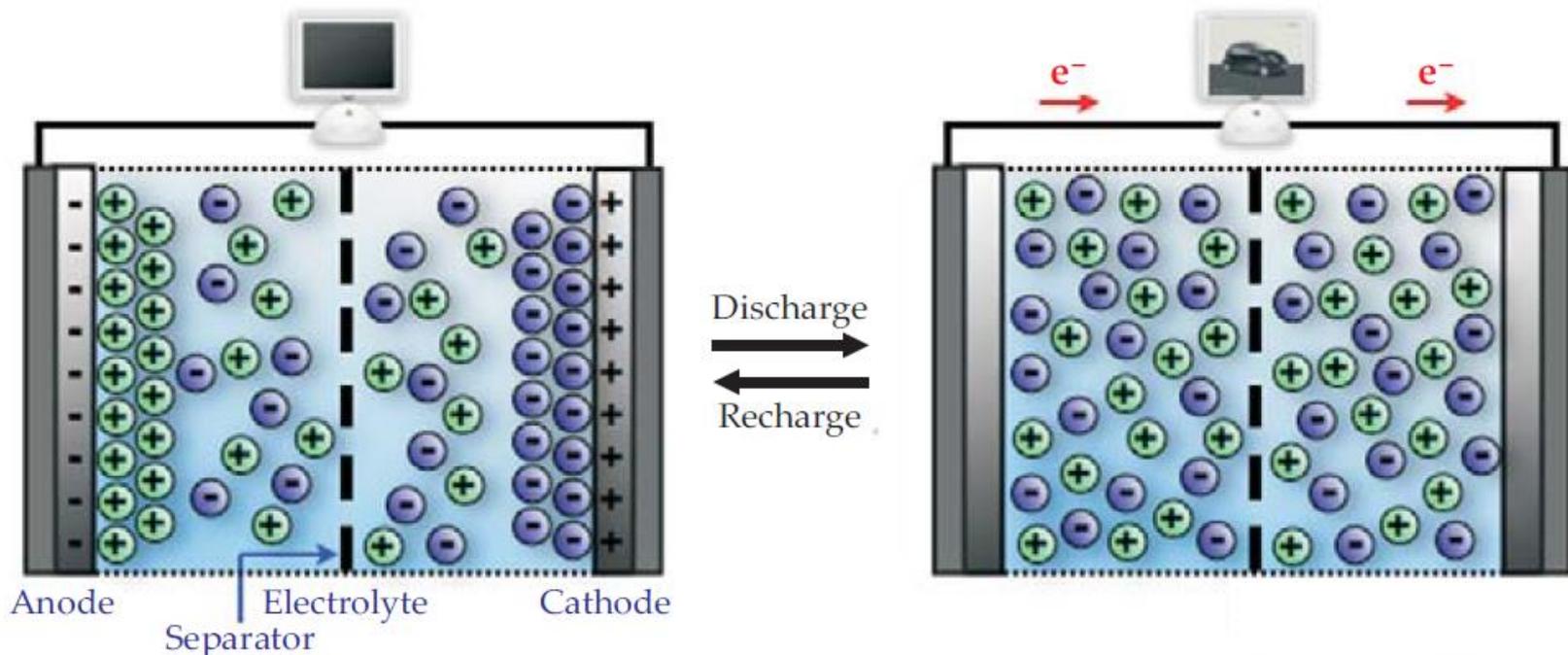
Filed April 14, 1954

Fig. 1.



# Energy Storage Mechanism of EDLCs

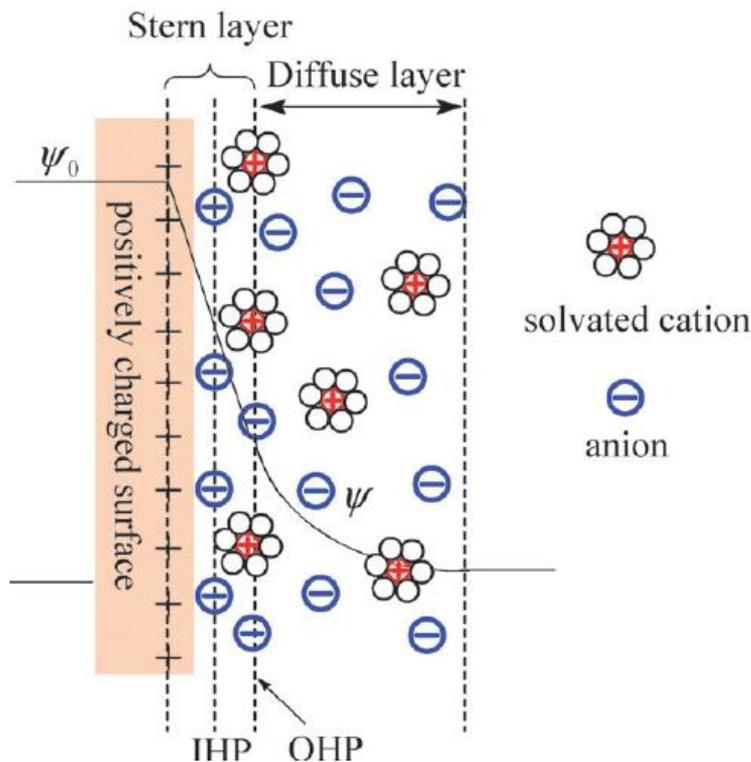
Electrosorption of ions (reversible potential-induced adsorption) at a high surface area electrode



H.D. Abruña, Y. Kiya, J.C. Henderson, *Phys. Today*, 61 (2008) 43.

Not limited by faradaic charge transfer or solid state mass transfer!

# Storing Charge at the Electric Double Layer



## Capacitance:

$$C = \epsilon_r \epsilon_0 \frac{A}{d} = \frac{Q}{V} = \frac{[\text{Coulomb}]}{[\text{Volt}]} = [\text{Farad}]$$

**A:** electrode surface area

**d:** distance b/w electrode & electrolyte, ~ few Å

**C:** 5 – 20  $\mu\text{F}/\text{cm}^2$ , < 100 F/g

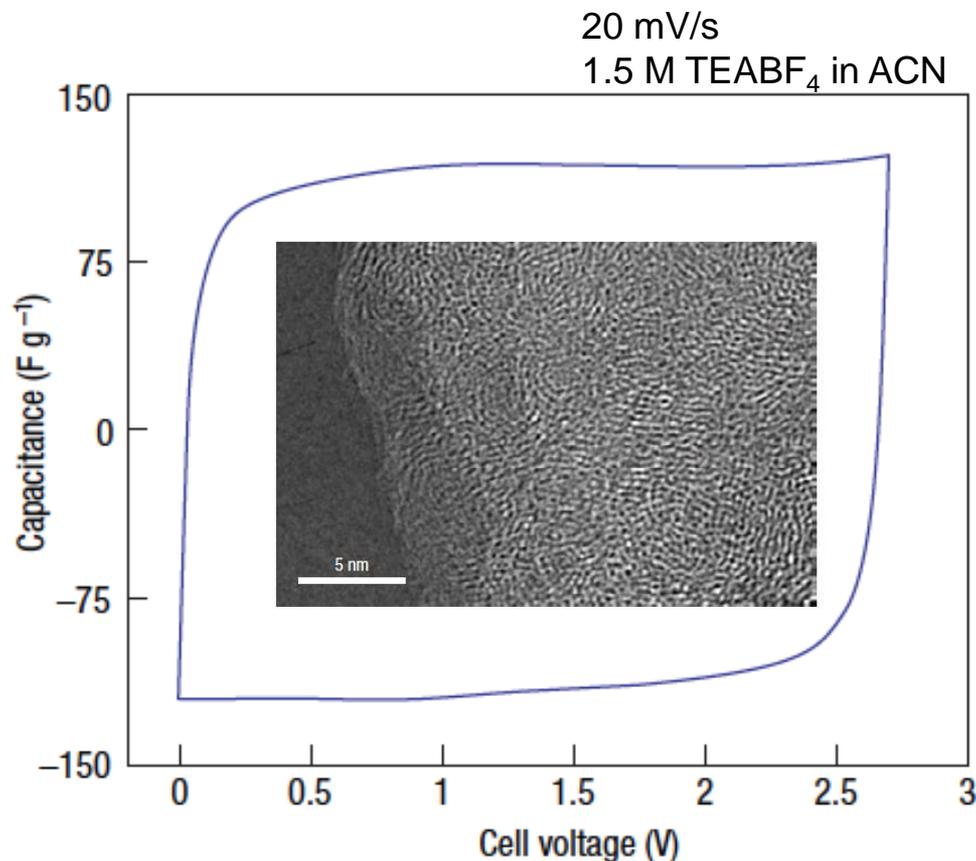
# Electrochemical Features of Carbons in EDLCs

## Why carbon?

- Relatively high conductivity
- Large surface areas
- Low density
- Good corrosion resistance
- Inexpensive

## For EDLCs:

- Surface area  $\sim 1000 \text{ m}^2/\text{g}$
- Good intra- & inter-particle conductivity
- Good electrolyte wetting
- Surface free of impurities to prevent self-discharge

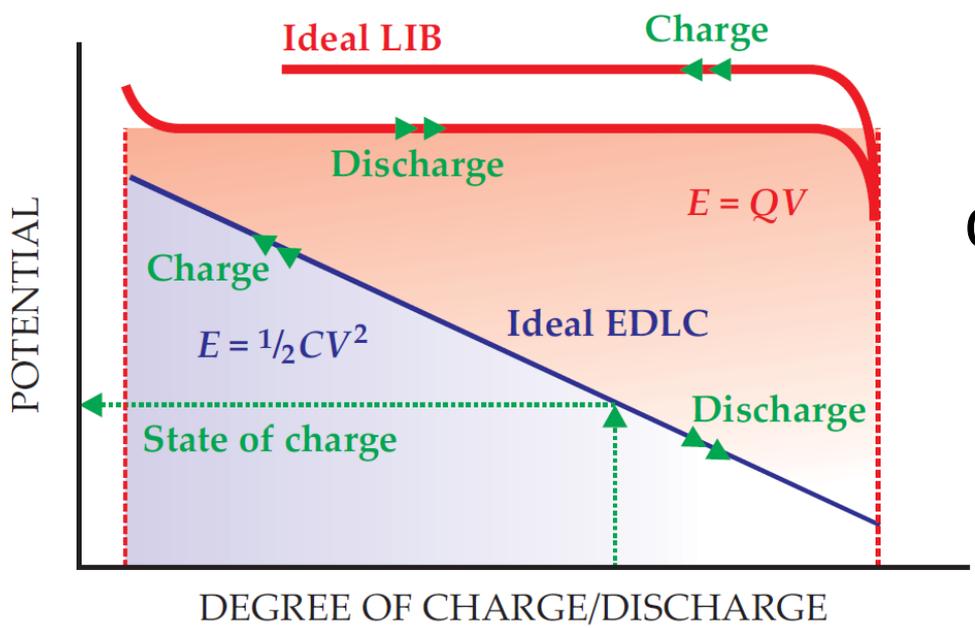


P. Simon & Y. Gogotsi, *Nature Mater.* 7 (2008) 845

B.E. Conway. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*. Kluwer, 1999.

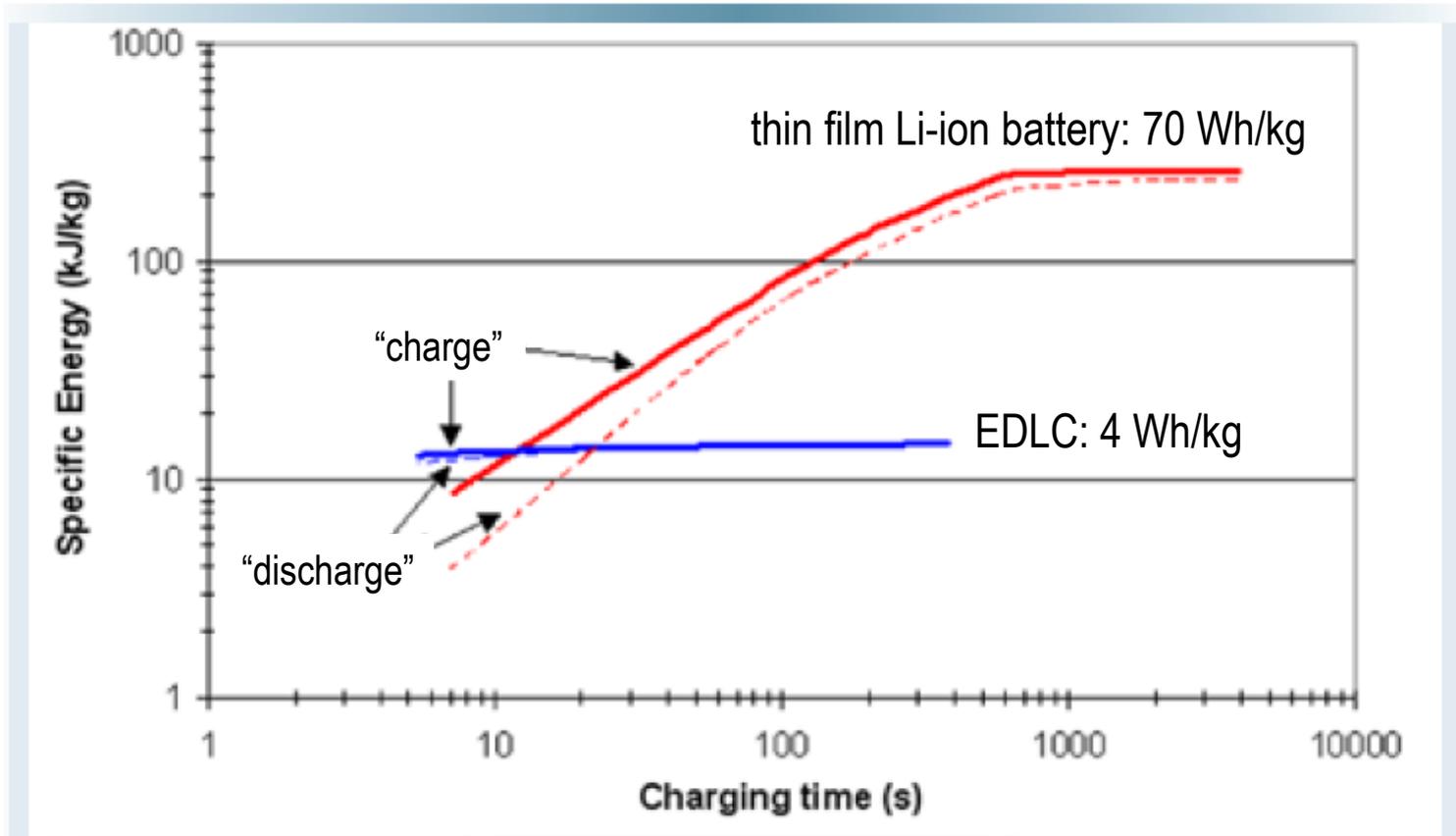
# Energy Storage of Batteries vs. EDLCs

Battery	EDLC
Ideally constant discharge curve	Intrinsically sloping discharge curve
May not have good state-of-charge indication	Good intrinsic state-of-charge indication
Higher energy density	Lower energy density
Lower power density	Higher power density
Cycle life limited by redox irreversibility & phase changes	Electrosorption leads to excellent cyclability



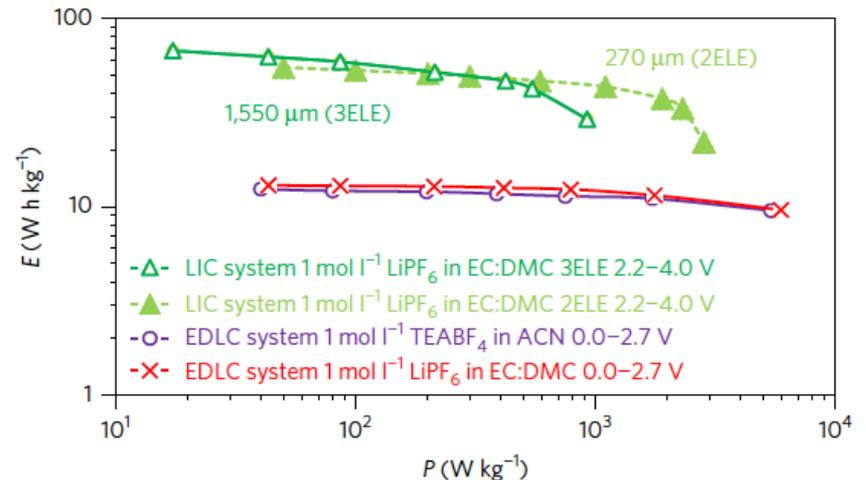
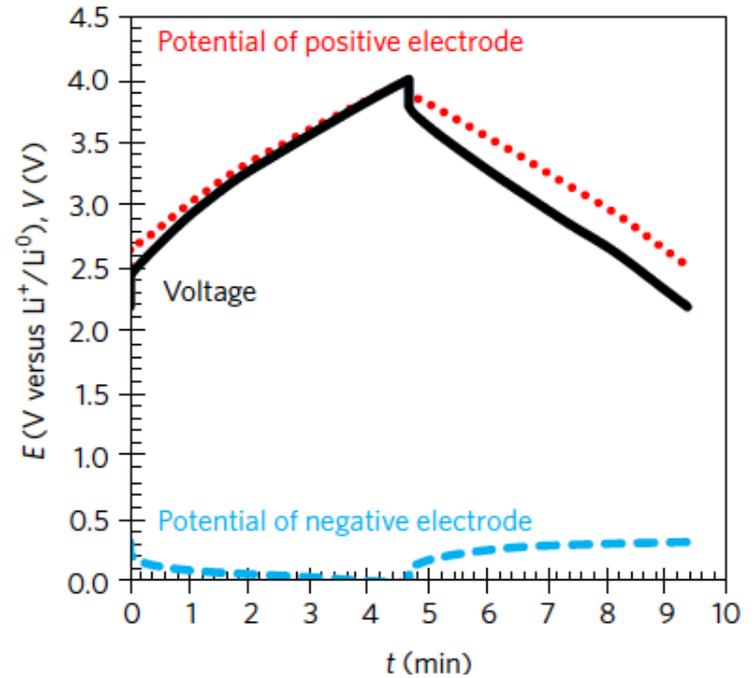
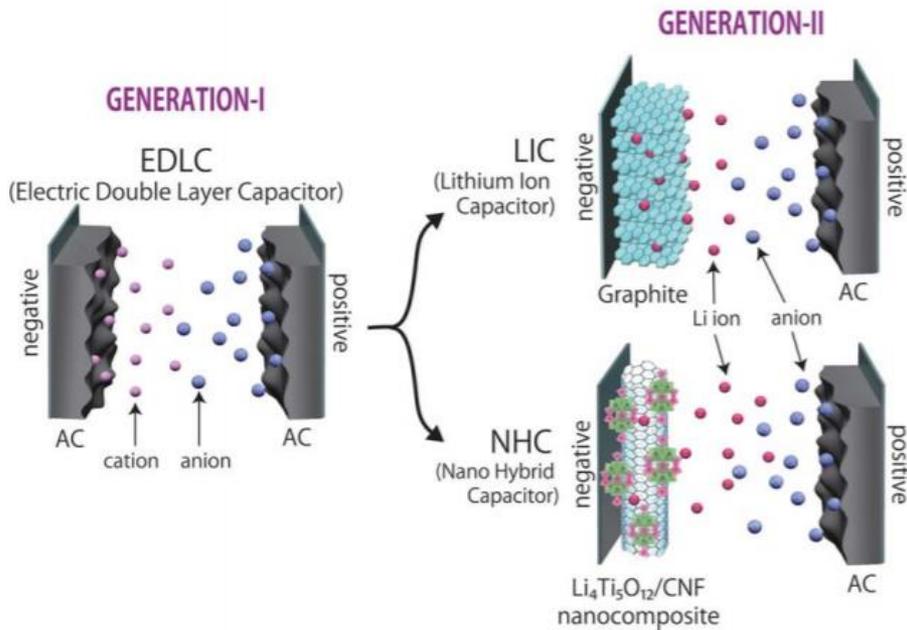
**Capacitance** of an ideal EDLC is constant:

# Energy Storage of Batteries vs. EDLCs



J.R. Miller & A.F. Burke, *Electrochem. Soc. Interface*, Spring 2008, 53.

# Hybrid Devices: Combining EDLCs with Faradaic Electrodes



P. Jeżowski, T. Brousse., et al., *Nature Mater.*, 17 (2017) 167.

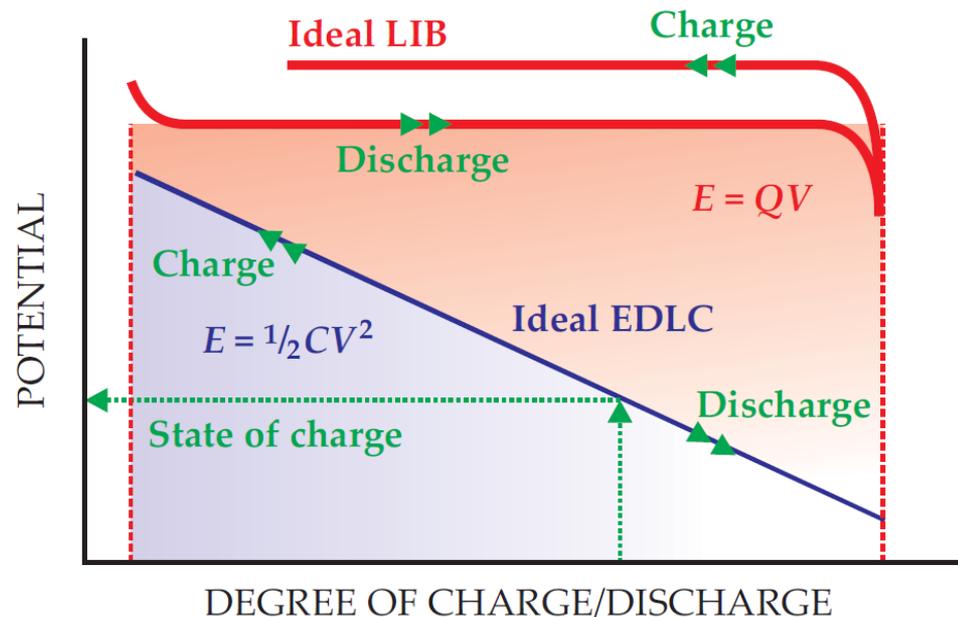
K. Naoi, et al., *Energy & Environ. Sci.*, 5 (2012) 9363.

# Increasing the Energy without Decreasing Power

$$\text{Energy} = \int_0^Q V dq = \frac{1}{2} QV = \frac{1}{2} CV^2$$

The energy can be increased by:

- the *capacitance/capacity* (electrode)
  - higher surface area carbons; pseudocapacitive materials (charge transfer via chemisorption, intercalation); pre-lithiated graphite
- the *voltage* (electrolyte)
  - wide potential window ionic liquids



# Pseudocapacitance

Reversible faradaic surface reactions (chemisorption) can significantly increase the areal, and thus gravimetric, capacitance

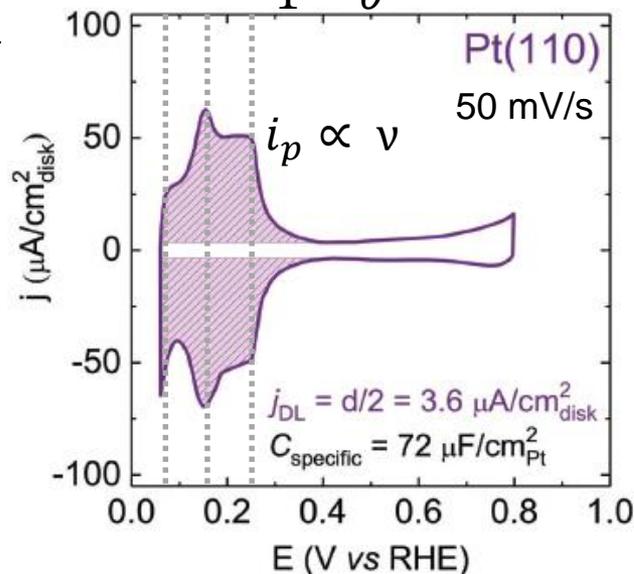
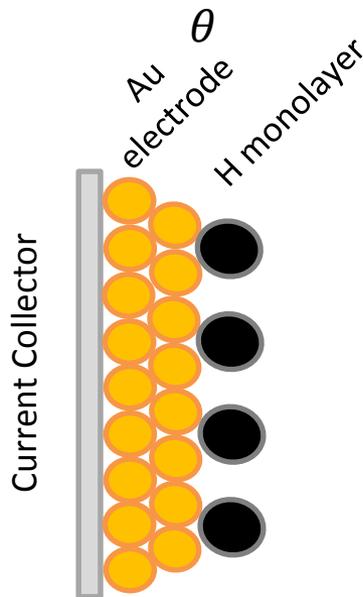
These processes are not limited by solid state mass transfer!

2D electrochemical chemisorption modeled as Langmuir or Frumkin isotherm:

formalism developed by Conway, Gileadi, & others in early 1960s

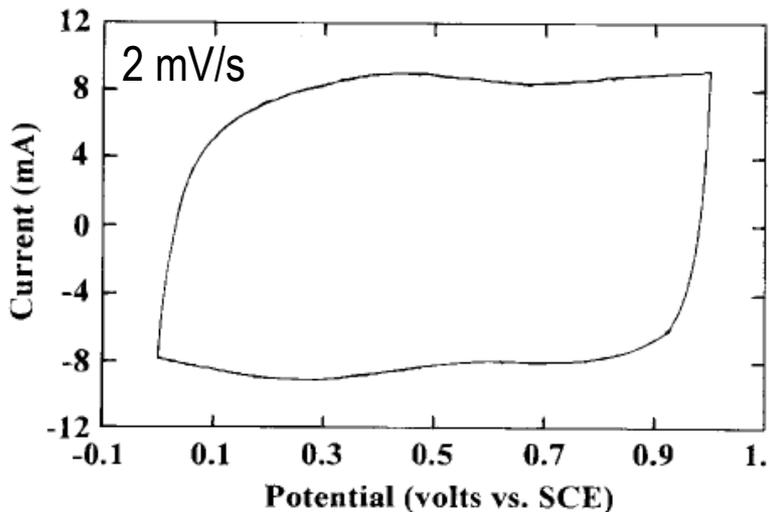


$$\frac{\theta}{1 - \theta} = KC_{\text{H}^+} e^{\frac{VF}{RT}} \quad C_P = q_1 \frac{d\theta}{dV}$$

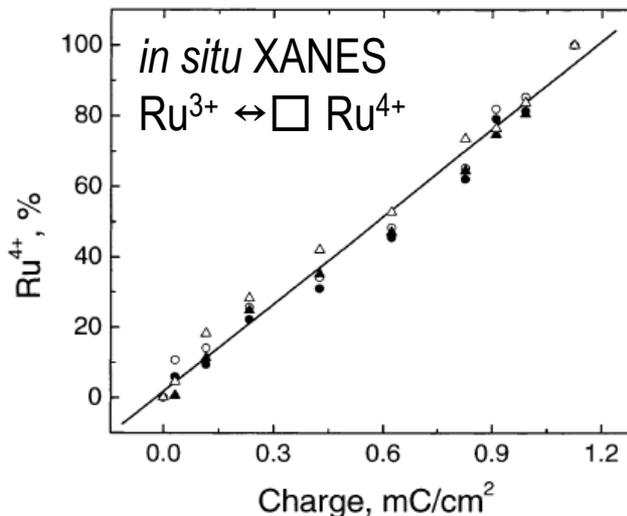


# Pseudocapacitance for Energy Storage: Hydrus RuO<sub>2</sub>

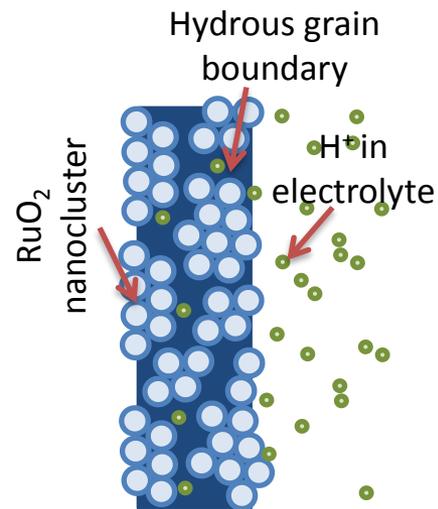
- First discovered by Trasatti & Buzzanca in 1971 when studying thin film and single crystal RuO<sub>2</sub> electrodes in acidic electrolyte *J. Electroanal. Chem. Interfacial Electrochem.* 29 (1971) App.1
- Appears capacitive but with huge surface area normalized capacitance
- Kinetics not limited by solid state mass transfer



J.P. Zheng, P.J. Cygan, & T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.



I.C. Stefan, D.A. Scherson, et al., *J. Phys. Chem. B* 106 (2002) 12373.



W. Dmowski, T. Egami, D.R. Rolison, et al., *J. Phys. Chem. B* 106 (2002) 12677.

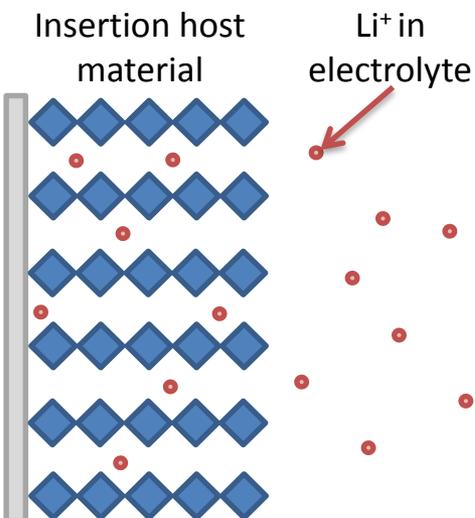
## RuO<sub>2</sub>·0.5H<sub>2</sub>O

Specific capacitance: 720 F/g

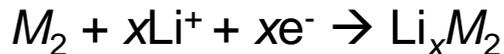
Areal capacitance: ~ 1,000 μF/cm<sup>2</sup><sub>BET SA</sub> (activated carbon: 3 – 70 μF/cm<sup>2</sup>)

# Intercalation Pseudocapacitance: Intercalation as Adsorption

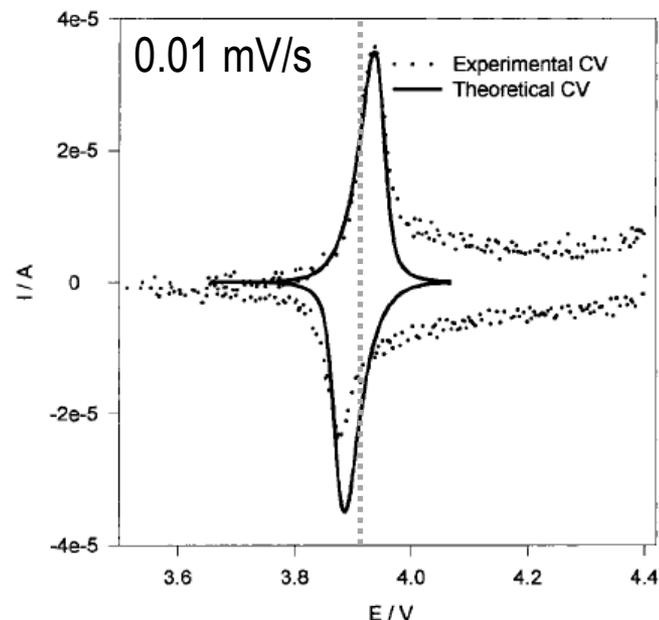
- Similarity between ion "sorption" into a bulk intercalation host and 2D adsorption at a surface
- Allows calculation of intercalation capacitance, analogous to pseudocapacitance
- Kinetics not considered "capacitive" due to sluggish solid state diffusion or phase transformations



## Frumkin intercalation isotherm



$$\frac{X}{1-X} = e^{\frac{VF}{RT}} e^{-g(X-0.5)}$$

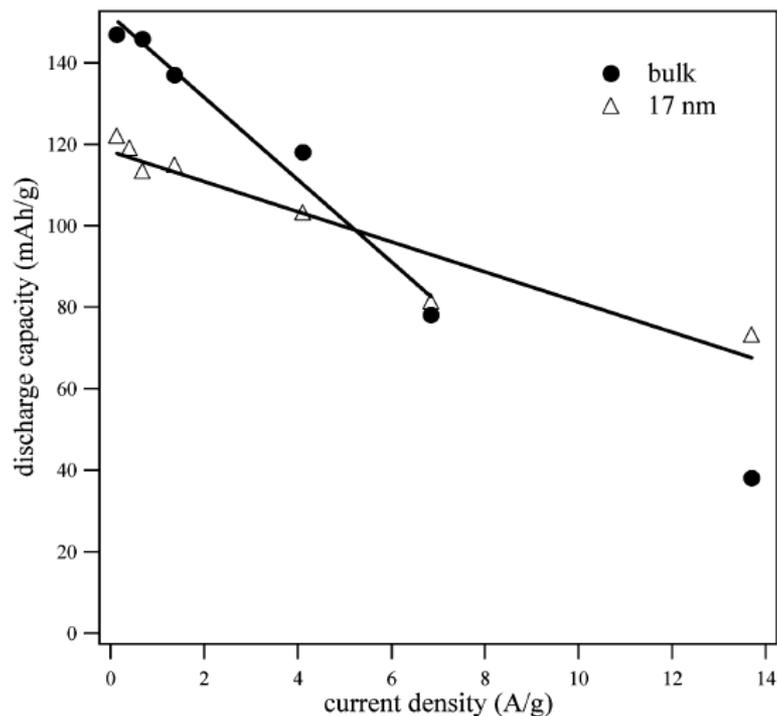


Li<sup>+</sup> intercalation into thin-film LiCoO<sub>2</sub>

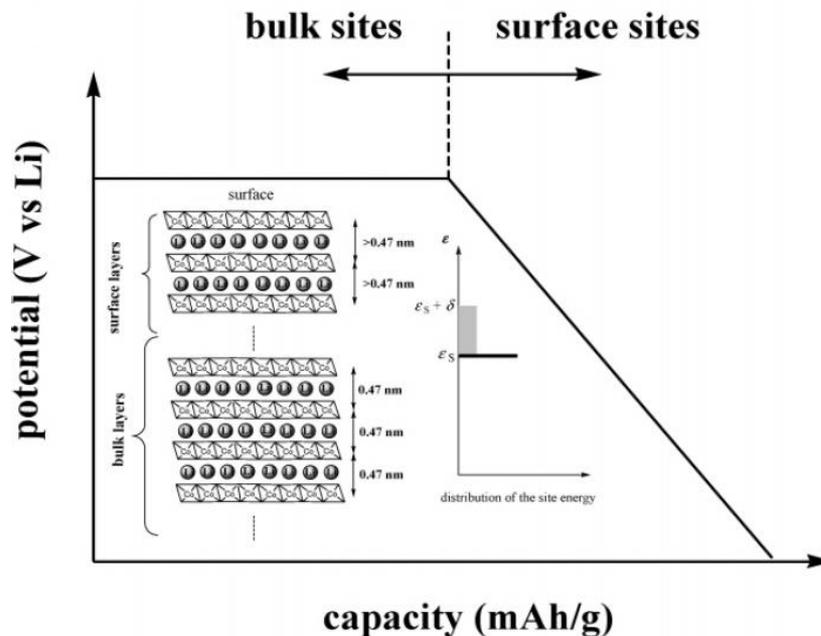
B. Conway, *Electrochim. Acta* 38 (1993) 1249.

M.D. Levi, D. Aurbach, *Electrochim. Acta* 45 (1999) 167.

# Capacitive Features of Li<sup>+</sup> Intercalation into Nanostructured LiCoO<sub>2</sub>



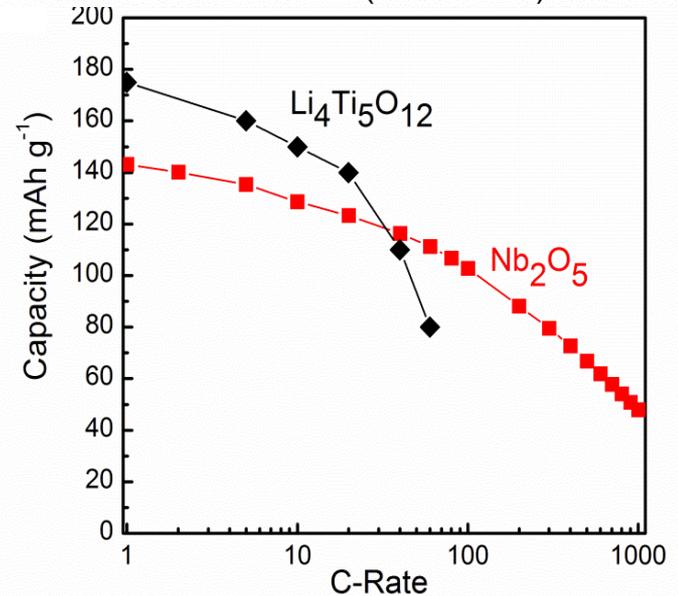
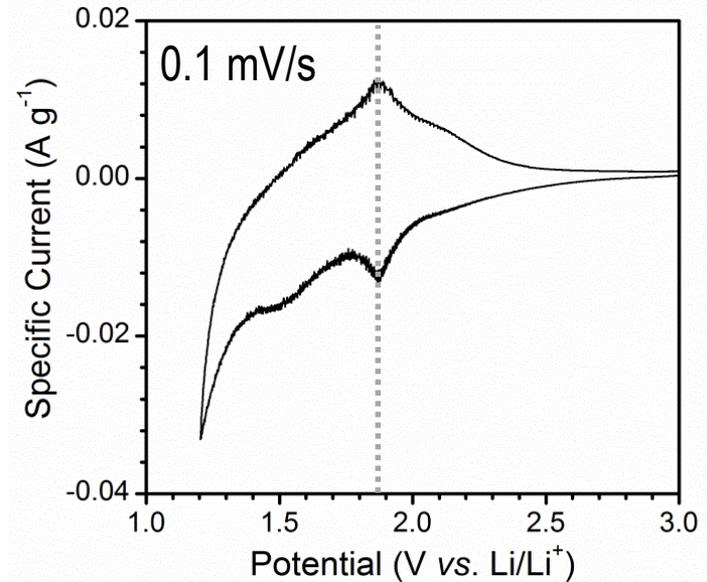
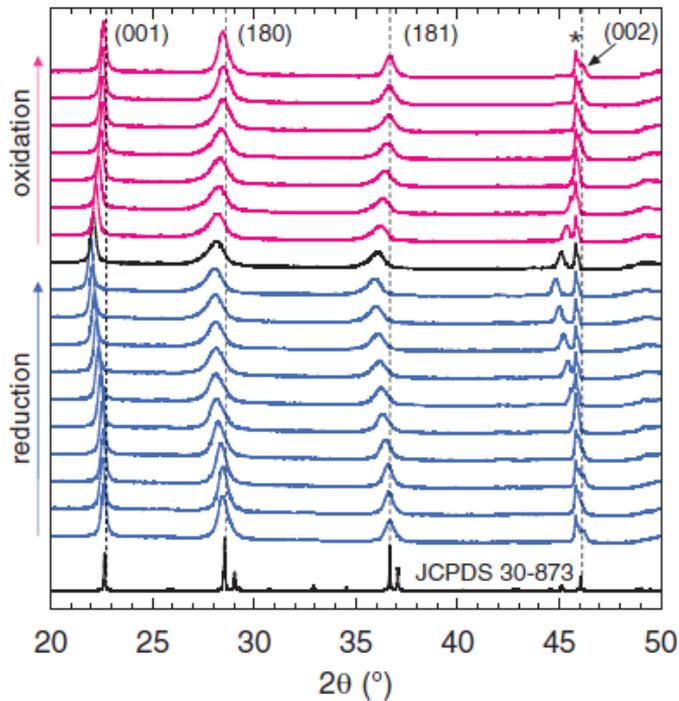
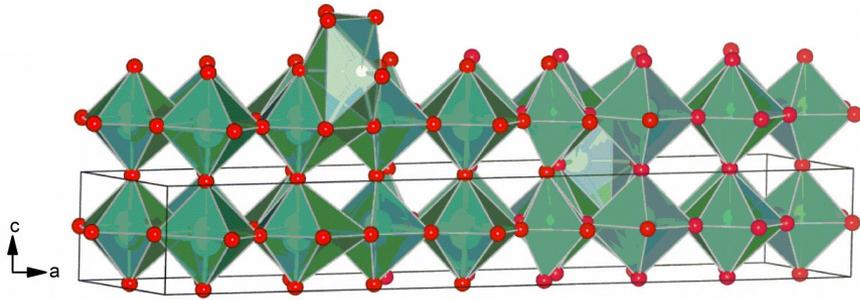
M. Okubo, I. Honma, et al., *J. Amer. Chem. Soc.* 129 (2007) 7444..



Concept of intercalation pseudocapacitance is important for achieving simultaneous high power + high energy density:

- Intercalation is a unique mechanism amongst batteries
- Recognizes mechanistic similarity between intercalation and surface adsorption
- **Gives pathway for “bulk” energy storage with surface-like kinetics**

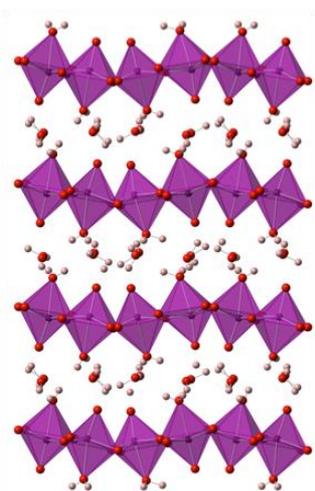
# Solid-Solution Intercalation into a Conductive Host: $\text{Li}_x\text{Nb}_2\text{O}_5$



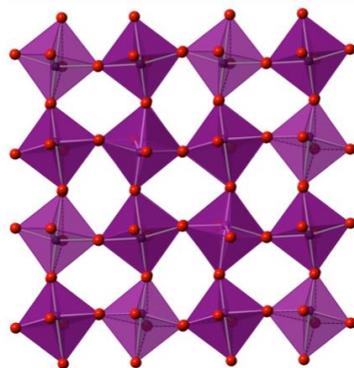
V. Augustyn, B. Dunn, et al., *Nature Mater.* 12 (2013) 518.

J. Come, P. Simon, et al., *J. Electrochem. Soc.* 161 (2014) A718.

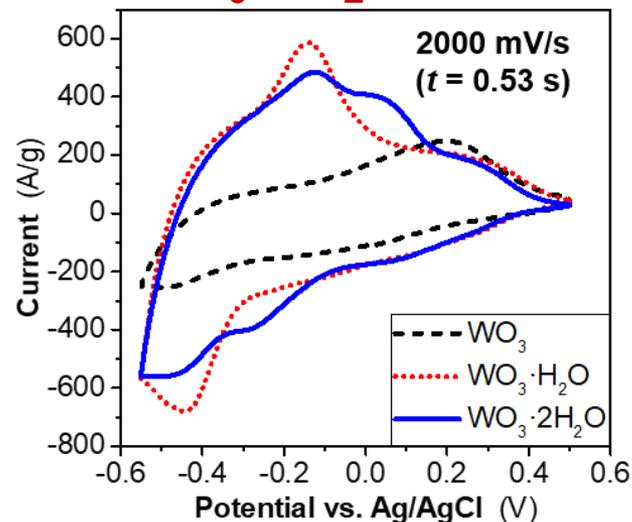
# Importance of Structural Stability for High Power: Proton Intercalation into $\text{WO}_3 \cdot n\text{H}_2\text{O}$



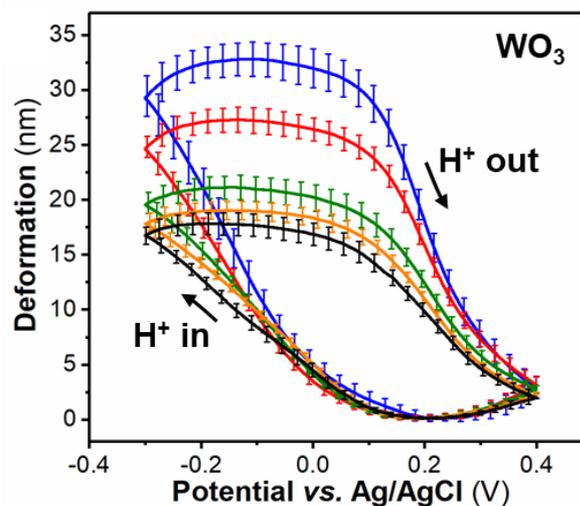
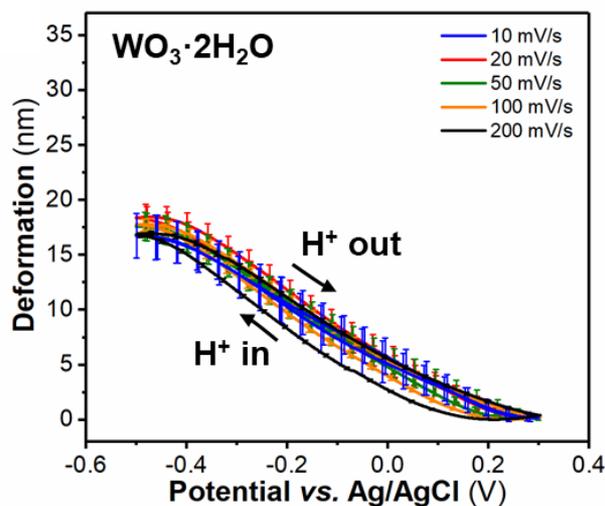
$\text{WO}_3 \cdot 2\text{H}_2\text{O}$



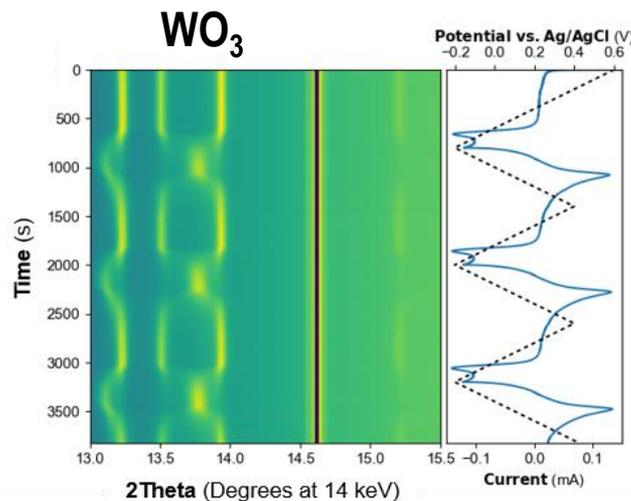
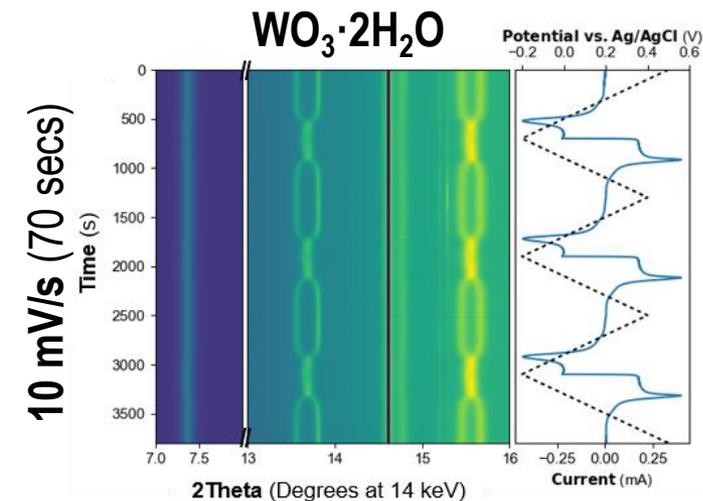
$\text{WO}_3$



*Operando* AFM dilatometry shows significant differences in intercalation-induced electrode deformation

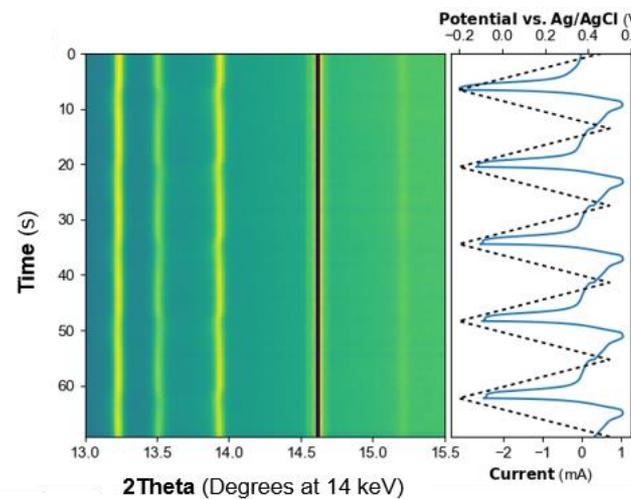
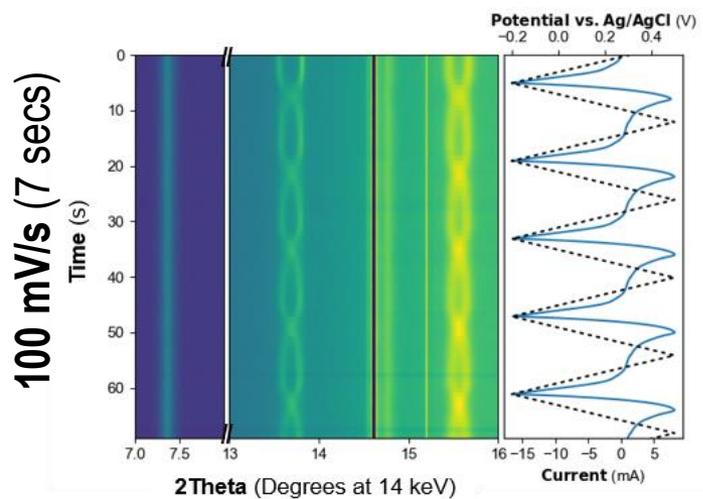


# Importance of Structural Stability for High Power: Proton Intercalation into $\text{WO}_3 \cdot n\text{H}_2\text{O}$



**At 10 mV/s (70 sec)**

- $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  exhibits rapid, reversible phase transition as a function of proton intercalation
- $\text{WO}_3$  does not completely transform, 2 phases present

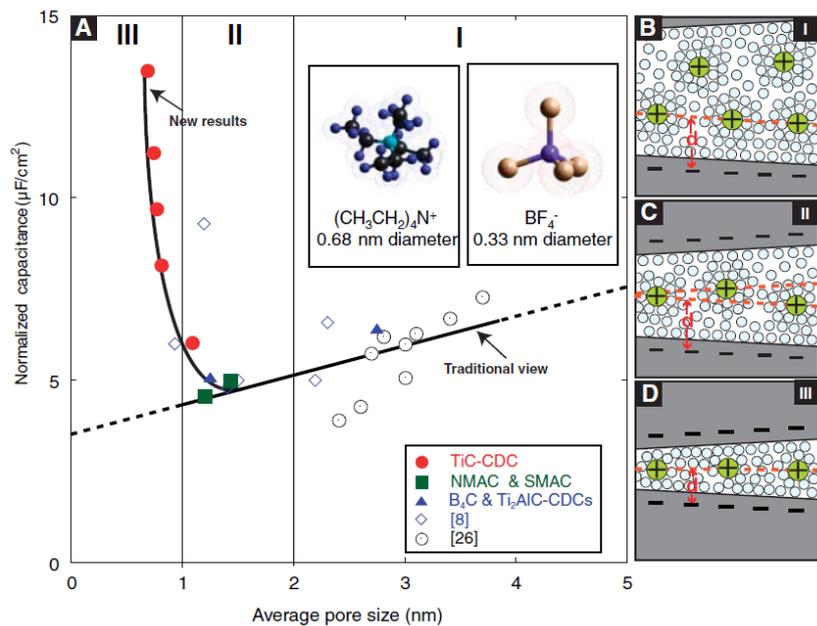


**At 100 mV/s (7 sec)**

- $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  still exhibits clear & reversible phase transition
- $\text{WO}_3$  appears “frozen,” structure not responding at this rate

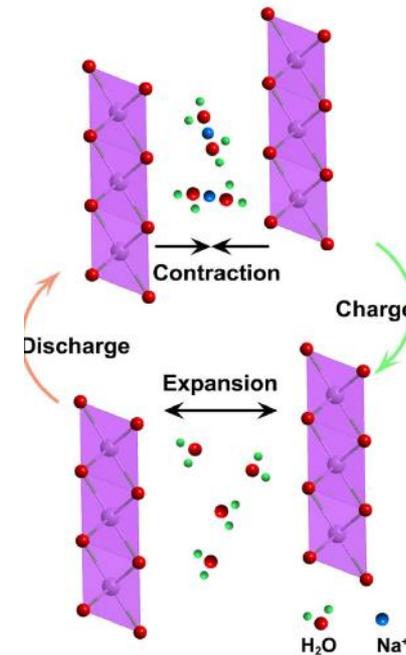
# Discriminating between Capacitive Mechanisms: Fundamental Nature of Nonfaradaic vs. Faradaic Processes

## Nonfaradaic: Capacitance in Sub-nm Pores



J. Chmiola, P.L. Taberna, et al., *Science* 313 (2006) 1760.

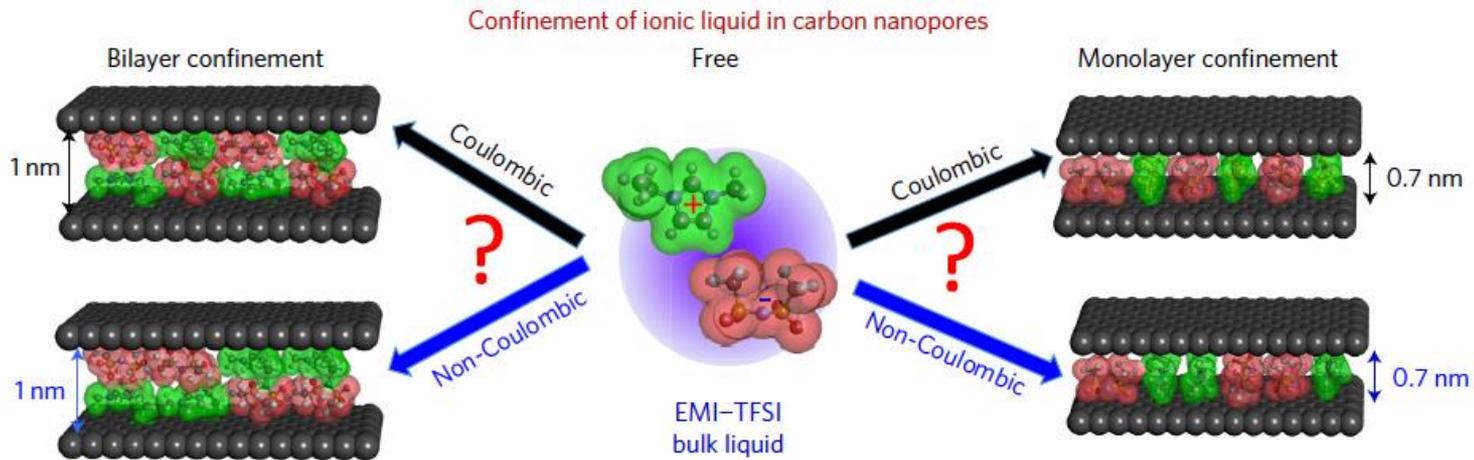
## Faradaic: Capacitance in Sub-nm Layers



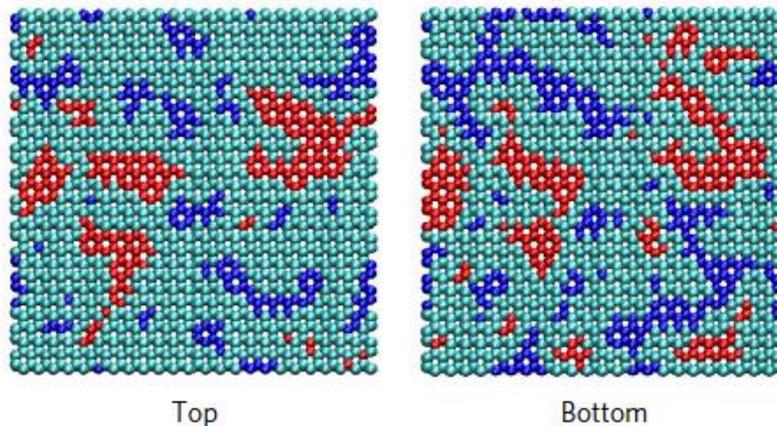
L. Yang, M. Liu, et al., *Nano Energy* 30 (2016) 293.

P. Simon, Y. Gogotsi, B. Dunn, *Science* 343 (2014) 1210.  
 T. Brousse, D. Bélanger, J.W. Long, *J. Electrochem. Soc.* 162 (2015) A5185.  
 Y. Gogotsi & R. Penner, *ACS Nano* 12 (2018) 2081.  
 Y. Liang & J. Liu, *Energy Environ. Sci.* 2 (2019) 30.  
 C. Costentin & J.M. Savéant, *Chem. Sci.* 10 (2019) 5656.

# Blurring the Line Between the Electrolyte and the Electrode: Capacitive Mechanisms Under Confinement



In 0.7-nm pore



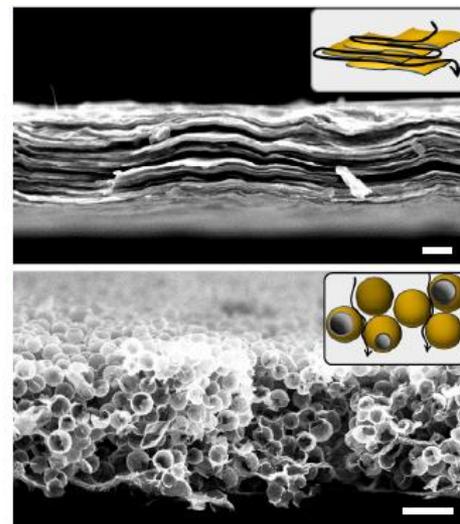
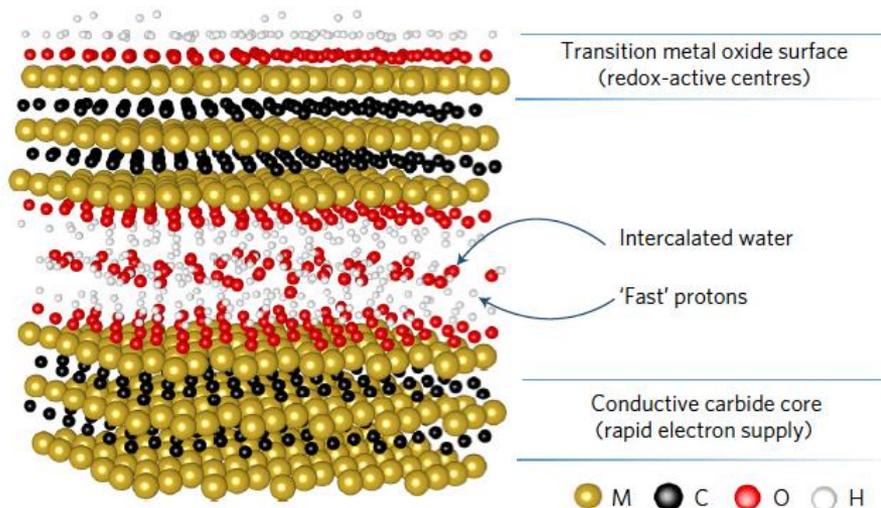
Simulated induced charges on carbon walls confining monolayer of ionic liquid:

blue: -0.01 eV

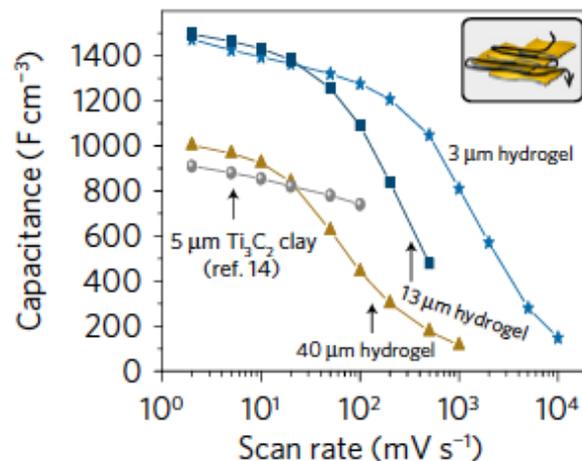
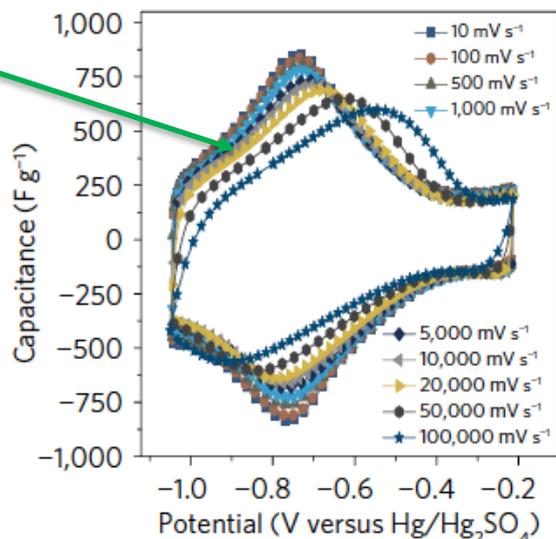
red: 0.01 eV

cyan: intermediate charge

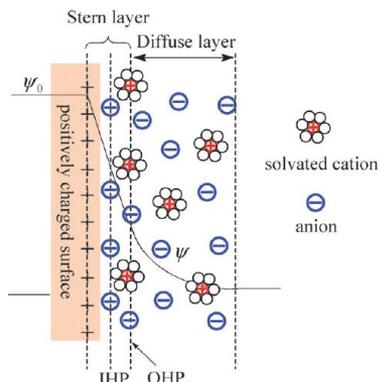
# Blurring the Line Between the Electrolyte and the Electrode: Proton Intercalation into $Ti_3C_2T_x$ MXene



10,000 mV/s =  
120 msec



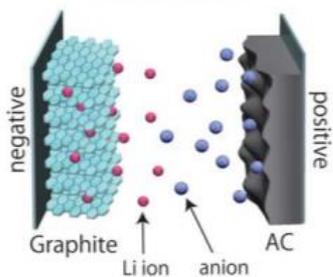
# Key Points



## Energy Storage at Electrochemical Interfaces

- Electrosorption & chemisorption of ions
- Excellent electrochemical reversibility
- No solid state mass transfer limitations

Chem. Soc. Rev. 38 (2009) 2520.



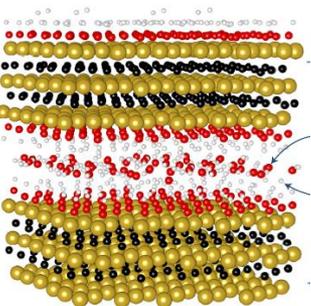
## Devices & Applications

- High power
- High reliability
- Complementary to batteries; take advantage of batteries for hybrid devices

Energy & Environ. Sci., 5 (2012) 9363.

## Emerging Materials & Concepts

- New materials & advanced characterization challenge traditional views of surface storage
- Insertion/intercalation processes critical for obtaining simultaneous high energy + high power
- Understanding confinement is crucial



Nature Energy 2 (2017) 17105.

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**Simon Fleischmann**  
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## Collaborators

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Yury Gogotsi, Drexel  
De-en Jiang, UC Riverside  
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Alexander Kolesnikov, ORNL  
Eugene Mamontov, ORNL  
Matt Pharr, Texas A&M  
Volker Presser, INM Leibniz  
Patrice Simon, Université Paul Sabatier  
Mike Toney, SLAC



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DMR-1653827



Center for Nanophase  
Materials Sciences



Fluid Interface  
Reactions,  
Structures, &  
Transport  
(FIRST) EFRC



Stanford Synchrotron  
Radiation Lightsource