



Development of Electrode Architectures for High Energy Density Electrochemical Capacitors



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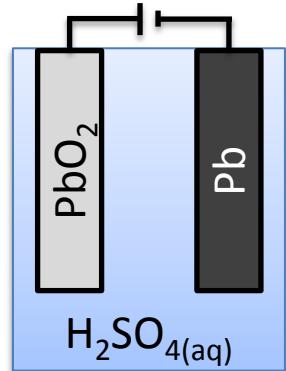
Electrochemical Energy Storage

Batteries

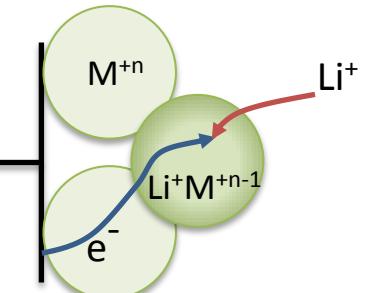
Diffusion Controlled

Faradaic Charge Storage (High Energy)

“Bulk”
Batteries



- e.g. Lead-Acid
- Charge stored in bulk
- Moderate Energy
- Low Power
- Low Cost



- e.g. Li-ion
- Charge stored in bulk
- High Energy
- Moderate Power
- Moderate Cost

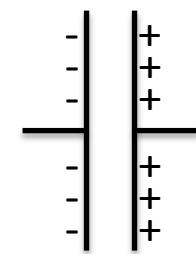
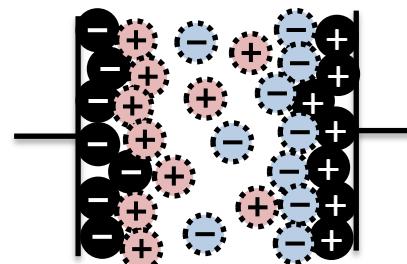
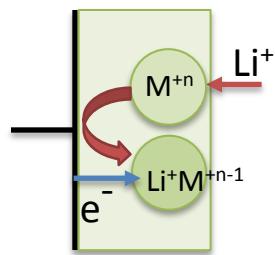
Capacitors

Non-Diffusion Controlled (High Power)

Non-Faradaic (Low Energy)

EC Double Layer
Supercapacitors

Capacitors



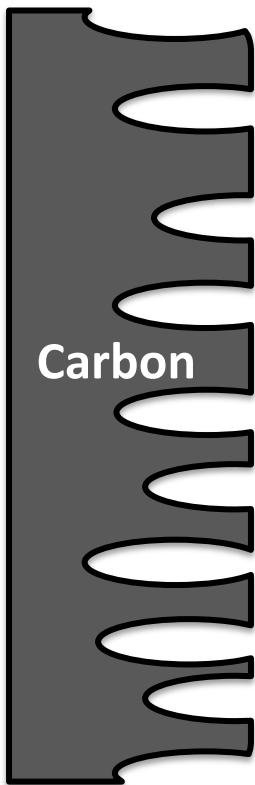
- Carbon
- Charge stored at surface
- Low Energy
- High Power
- Low Cost

- Metal
- Charge stored at surface
- **Low Energy**
- **High Power**
- Low Cost

Pseudo- vs. Supercapacitors

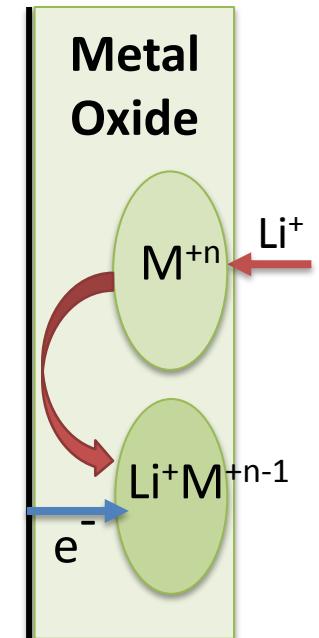
EC Double Layer Supercapacitor

- Moderate Energy
- High Power
- High surface area



Pseudocapacitor

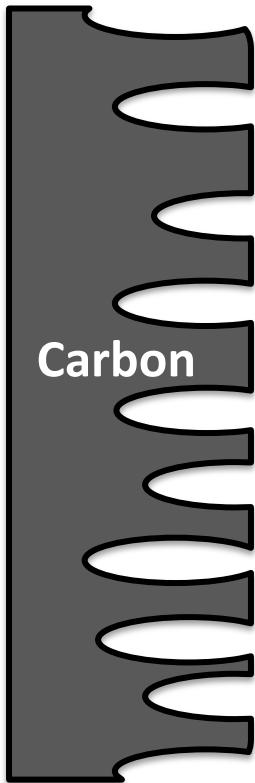
- Moderate Energy
- High Power
- Very thin (nm)



Pseudo/Supercapacitor Composite

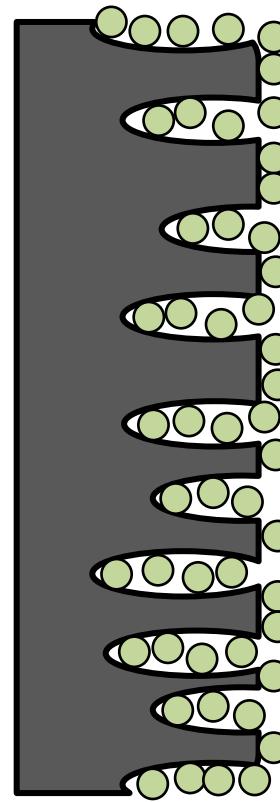
EC Double Layer Supercapacitor

- Moderate Energy
- High Power
- High surface area



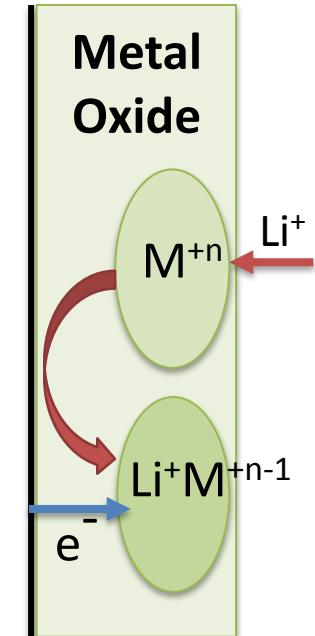
Metal Oxide / Carbon Composite

- High Energy
- High Power



Pseudocapacitor

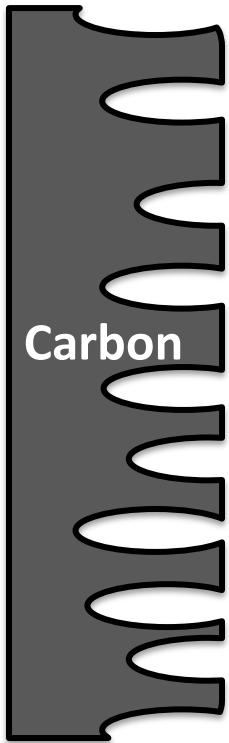
- Moderate Energy
- High Power
- Very thin (nm)



UCLA - Drexel Collaboration

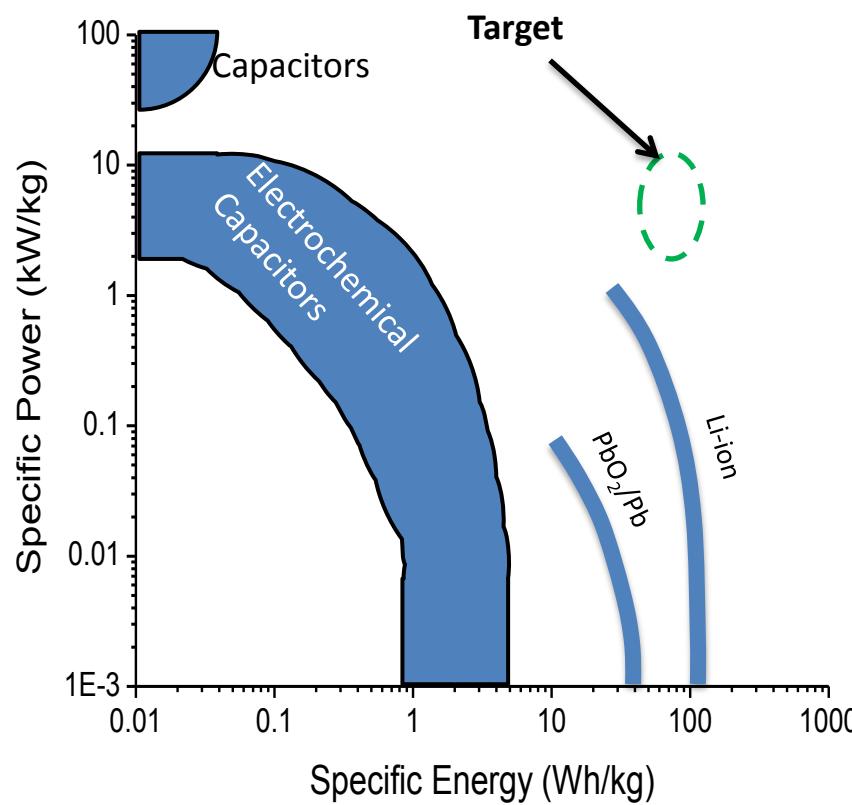


- Carbide-derived Carbon
- Coin-cell fabrication
- Device characterization

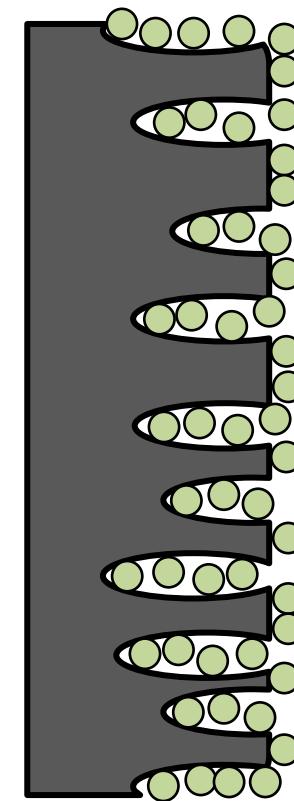


Project Goals

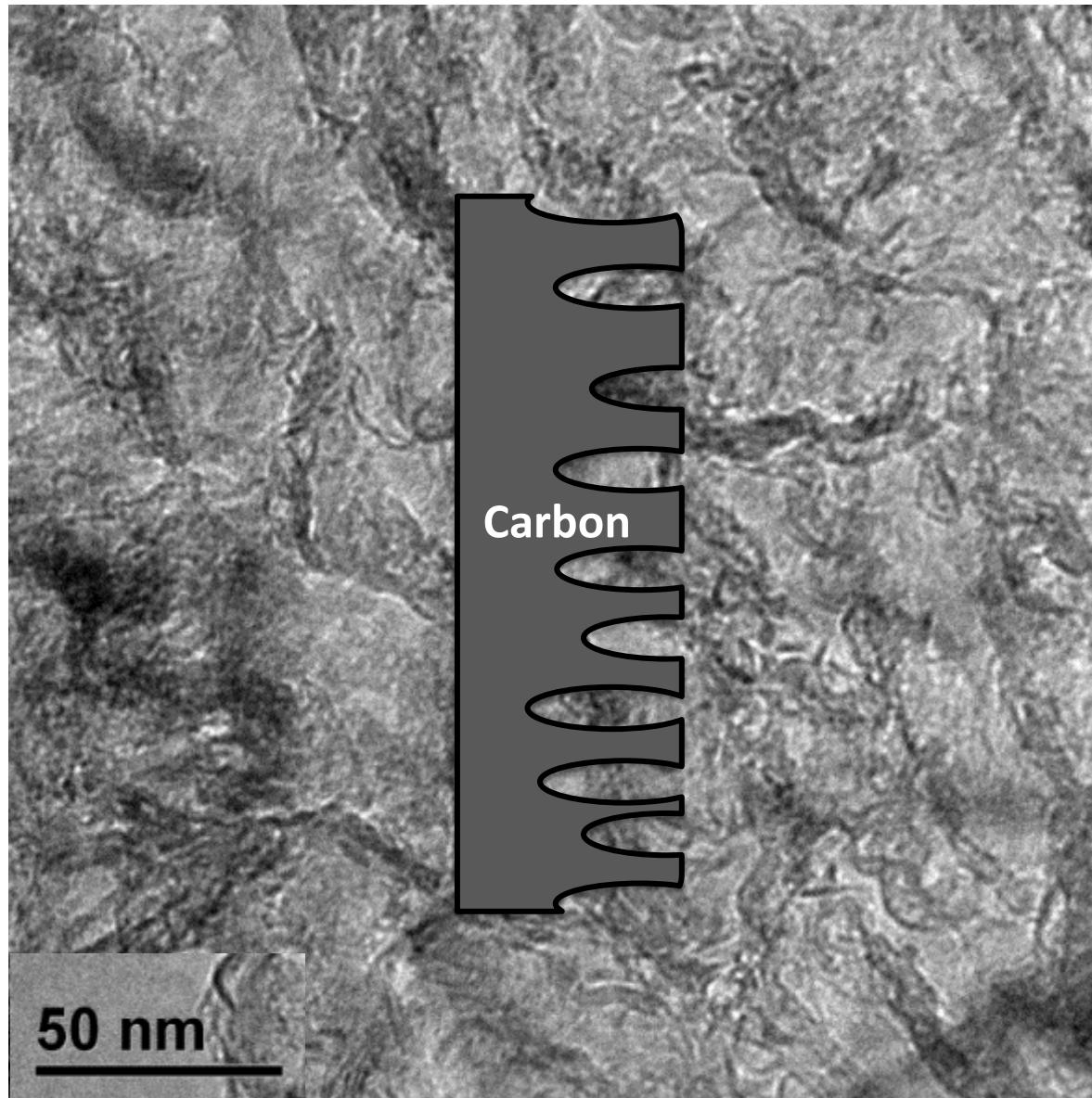
DOE Office of Electricity
Energy Storage Systems Program
University Energy Storage Program
100 Wh/kg, 1-10 kW/kg



- Metal-oxide deposition
- Small-scale testing
- Materials characterization

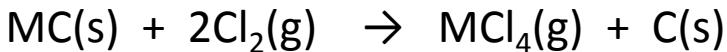


Supercapacitive Carbon

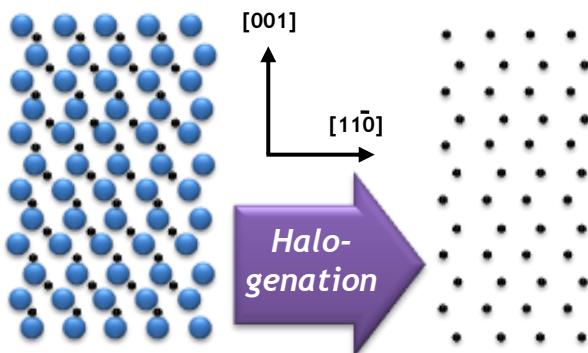
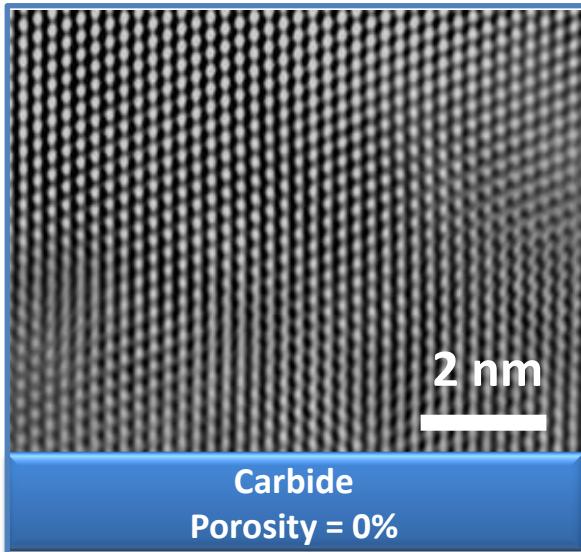


Supercapacitor: Carbide-Derived Carbon

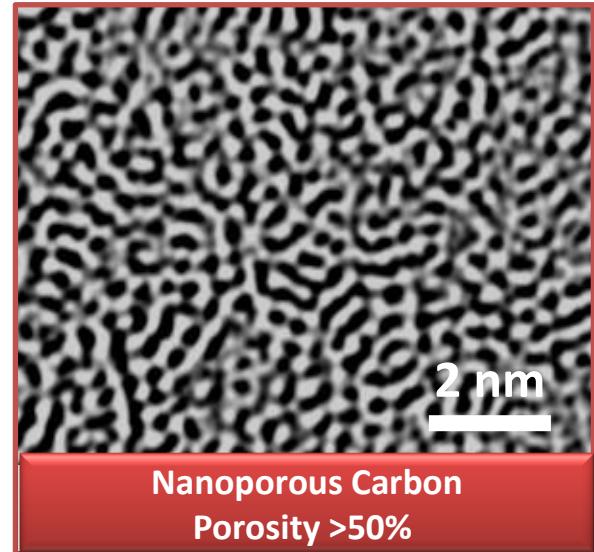
Carbide → Chlorination → Carbon



Carbide

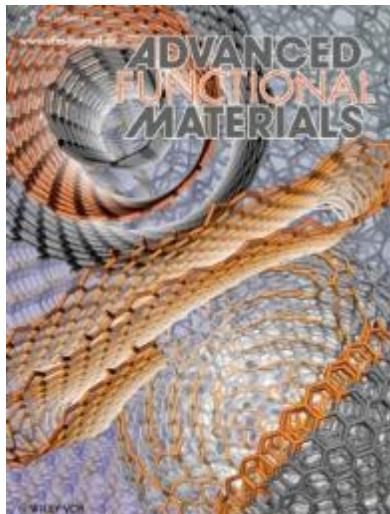


Carbide-Derived Carbon



Process Features

- Precise control over structure and porosity / pore size / surface area
- Network of open pores
- Coatings, free standing monoliths, fibers, foams or powder
- Numerous carbides can be used



O. Hutchins, US Patent, 1271713 (1918)
W.A. Mohun, US Patent, 3066099 (1962)

Nillok Chemicals, Great Britain Patent, 971943 (1964)

S.K. Gordeev et al., *J.Appl. Chem. (USSR)* 64, 1178 (1991)

N.F. Fedorov, *Russ. Chem. J.* 39, 73 (1995)

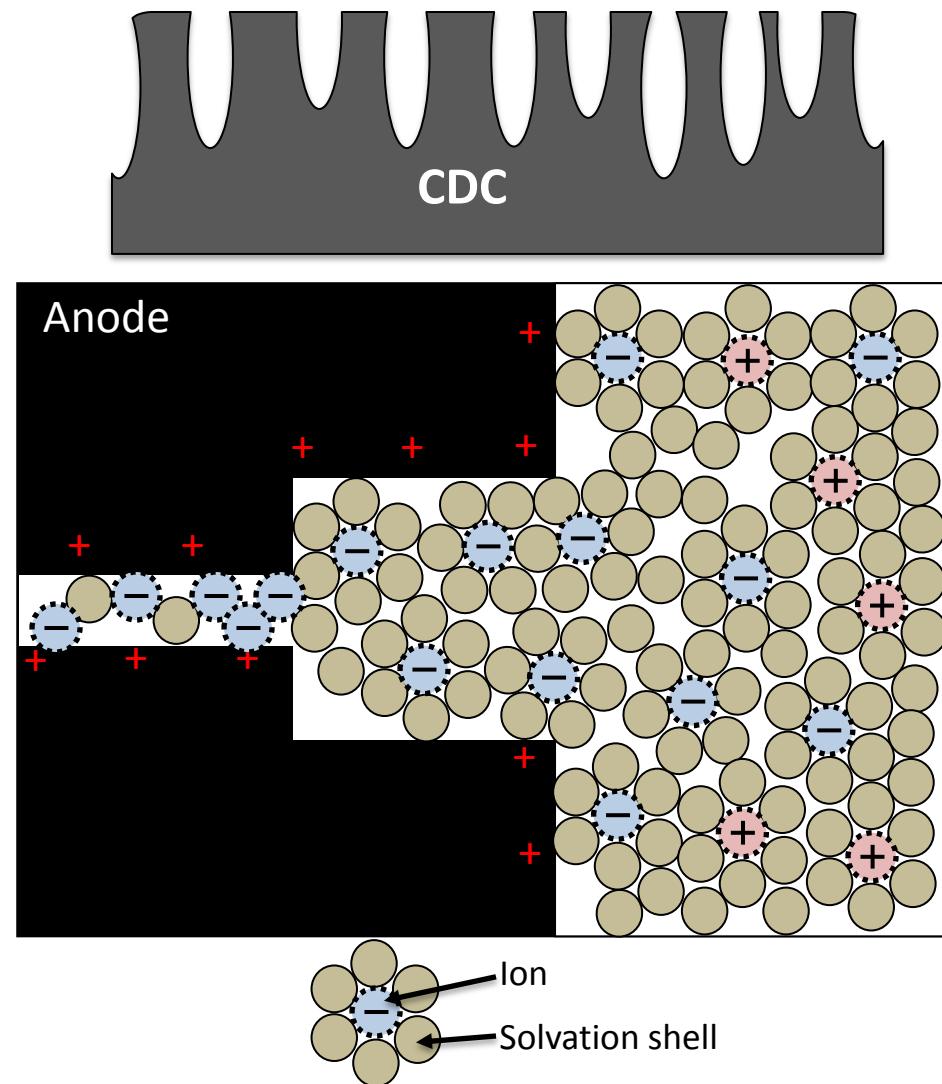
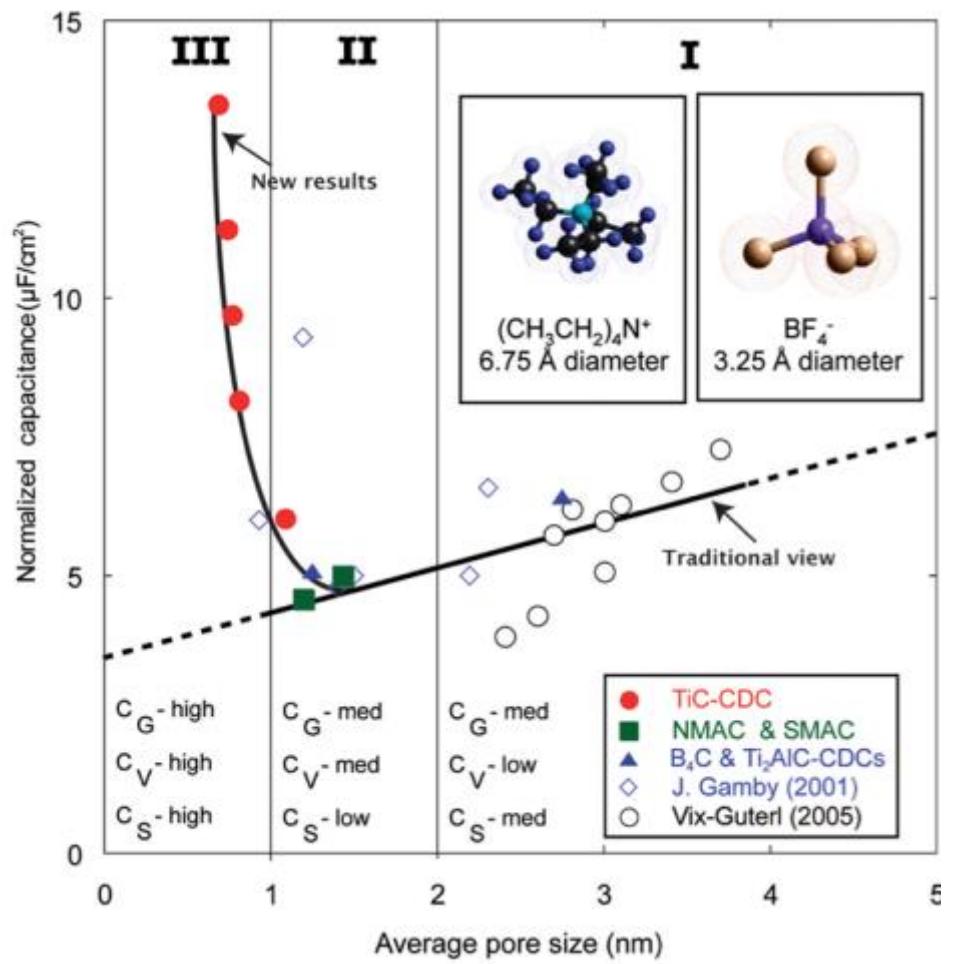
Y. Gogotsi, M. Yoshimura, *Nature*, 367, p. 628 (1994)

Y. Gogotsi, et al, *Nature*, 411, p. 283 (2001)

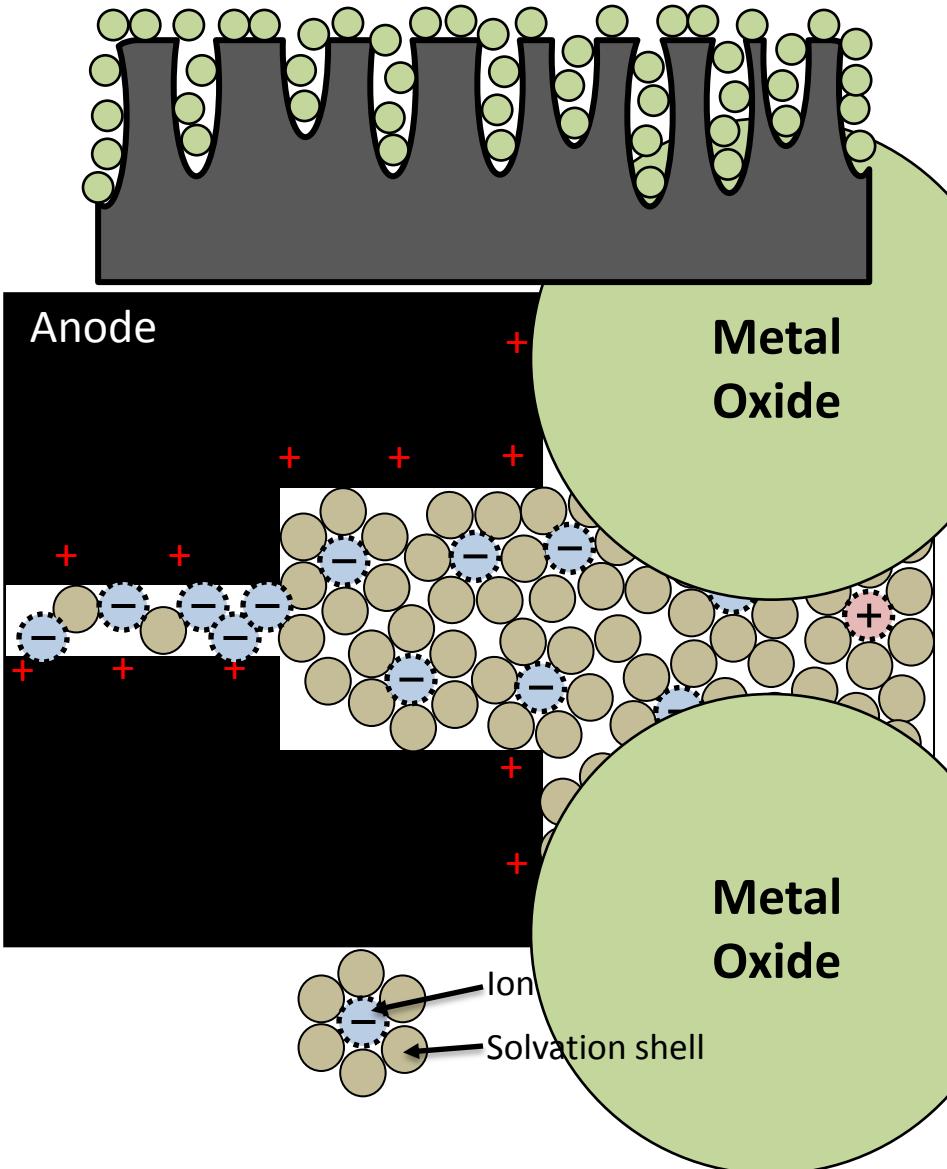
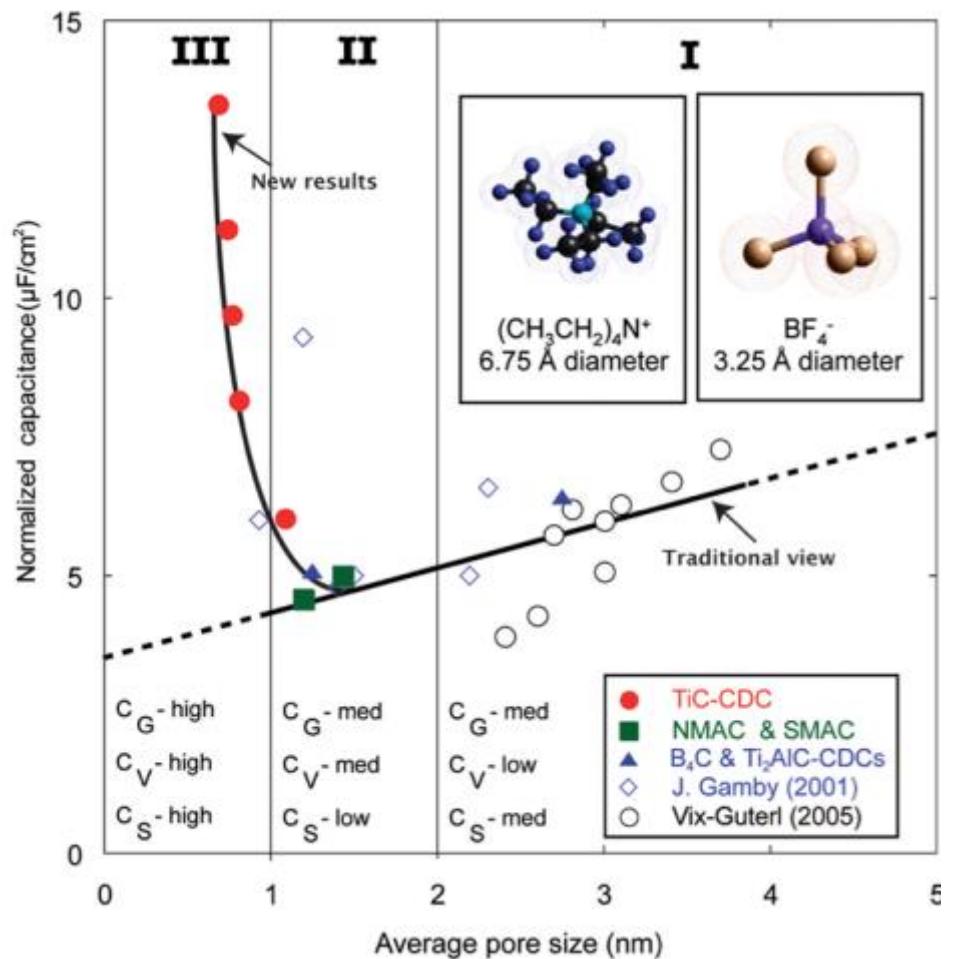
J. Leis, et al. *Carbon*, 39, 2043 (2001)

V. Presser, et al. *Advanced Functional Materials*, 21, 810 (2011).

Supercapacitor: Carbide-Derived Carbon

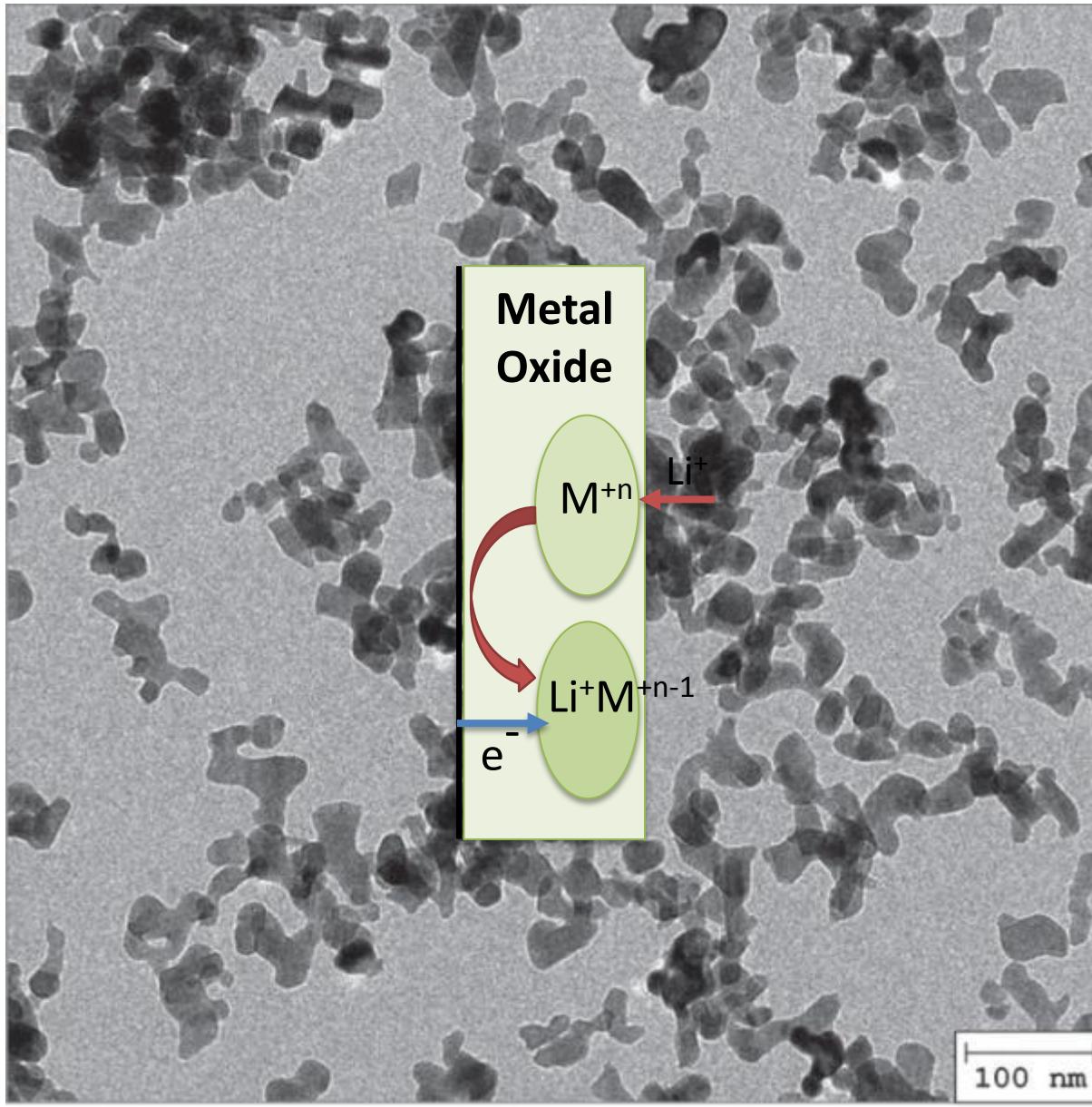


Supercapacitor: Carbide-Derived Carbon



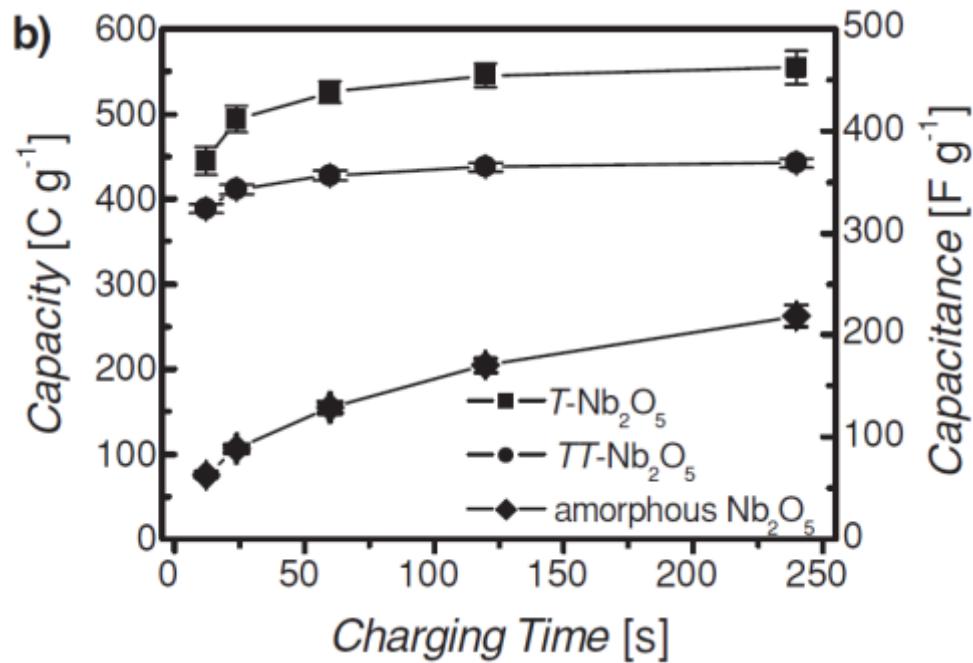
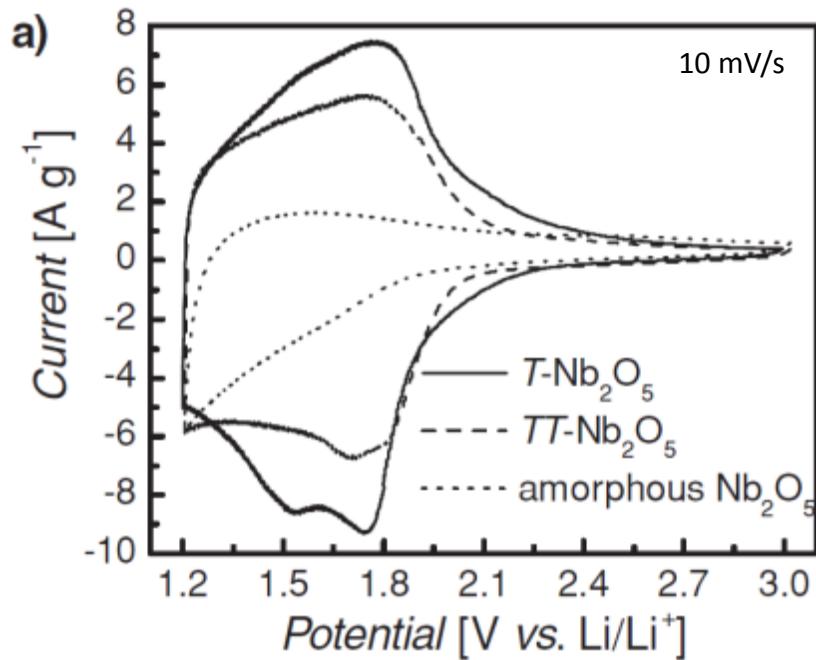
Pseudocapacitive Metal-oxide

UCLA



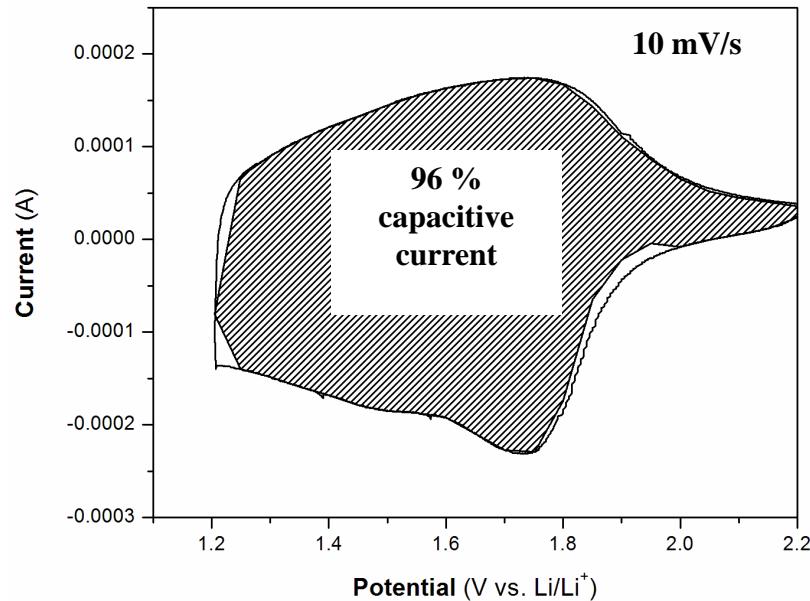
100 nm

Pseudocapacitor: Nb_2O_5



Kim et al., Adv. Energy Mat. 2, 141-148 (2011)

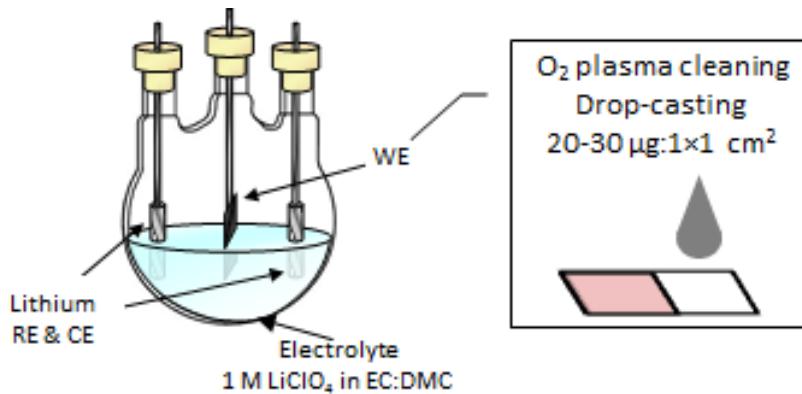
- Highest capacitance observed with most ordered structure:
 $T\text{-Nb}_2\text{O}_5$, ~ 370 F/g in 12 seconds
- Amorphous capacity is much smaller & slower
- Presence of an ordered structure is important to achieve high capacity
- (Almost) all of the stored charge is from pseudocapacitance



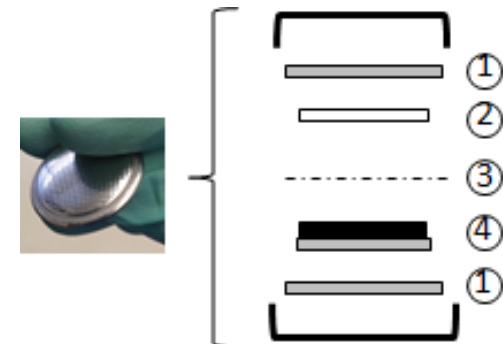
Electrochemical Characterization

Three-step process for developing electrode materials for supercapacitor devices

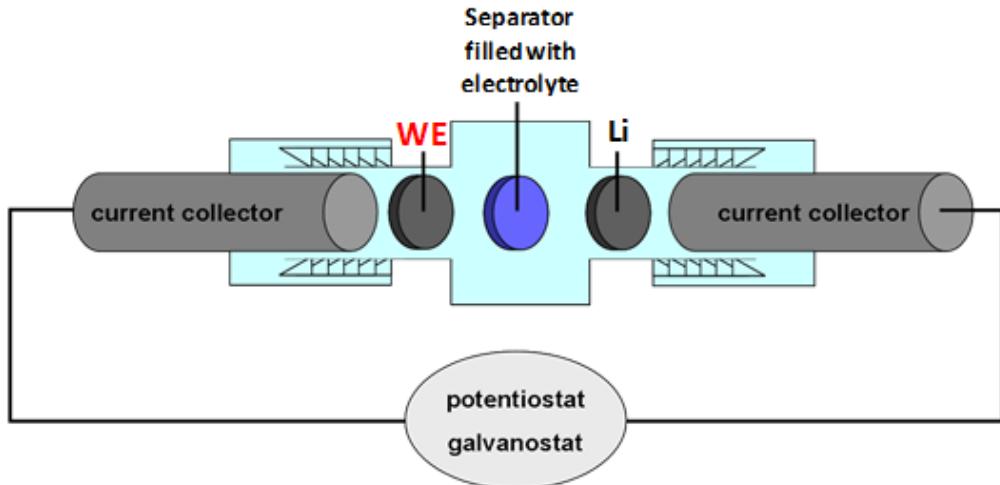
1. Nanocrystalline electrodes: no carbon or binder; half-cell experiments;
Designed to rapidly establish fundamental electrochemical properties



3. Coin Cells: Full cell prototype devices; symmetric and asymmetric



2. Swagelok cells: Practical electrode structure with carbon and binder. Half-cell experiments



Carbide-derived carbon/Nb₂O₅ hybrid materials

Ti₂AIC powder

1. Chlorination for 3 h at 800 °C

CDC powder

2. Hydrogenation for 2 h at 600 °C

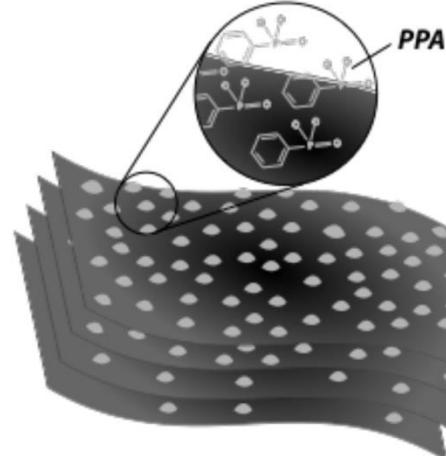
phenylphosphonic acid (PPA)

C₄H₉AlCl₂(C₆H₅COO)₂

Sonication

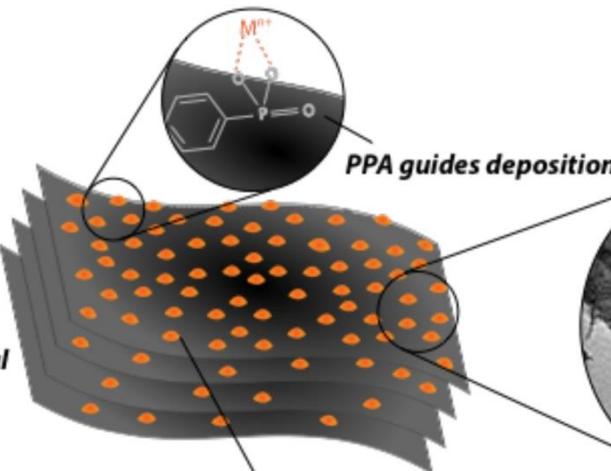
Hydrothermal treatment for 96 h at 200 °C

Nb₂O₅/CDC powder

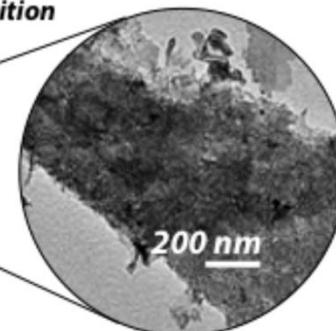


Hydrothermal treatment

PPA on CDC surface



Homogeneous Nb₂O₅/CDC



TAC-CDC with PPA

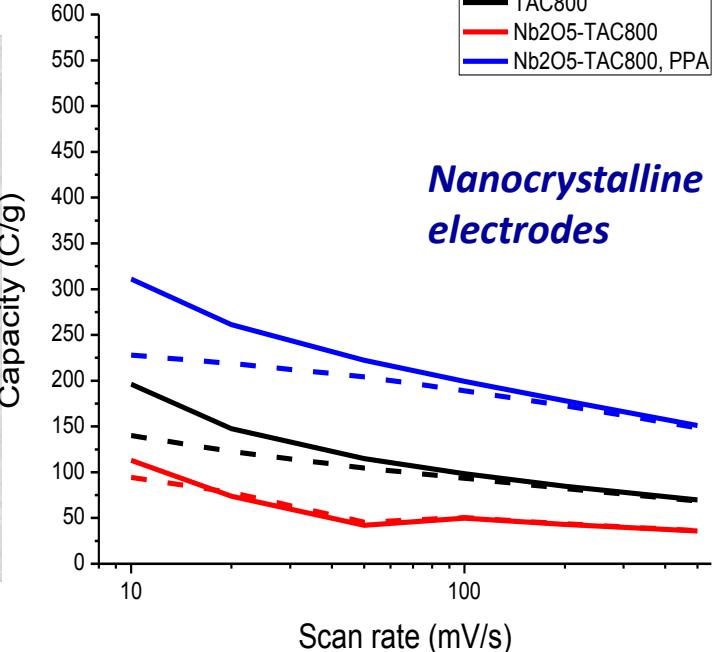
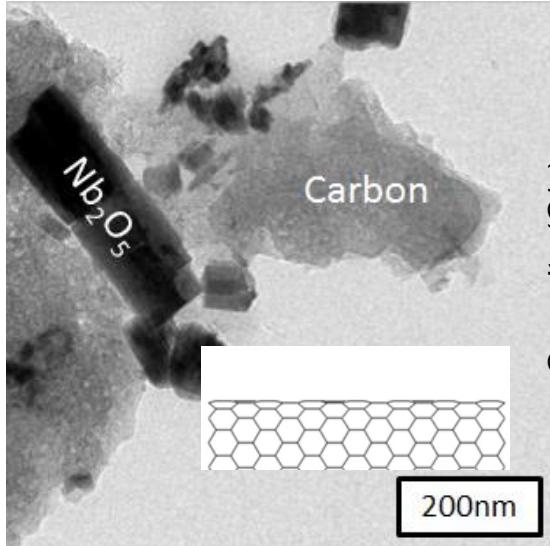
200 nm

Development of Nb_2O_5 /CDC Composite Electrodes

Without bonding agent

Carbon: TAC800
Metal-oxide: Nb_2O_5
Crystallinity: Amorphous
% oxide: 20%
Synthesis: Hydrothermal

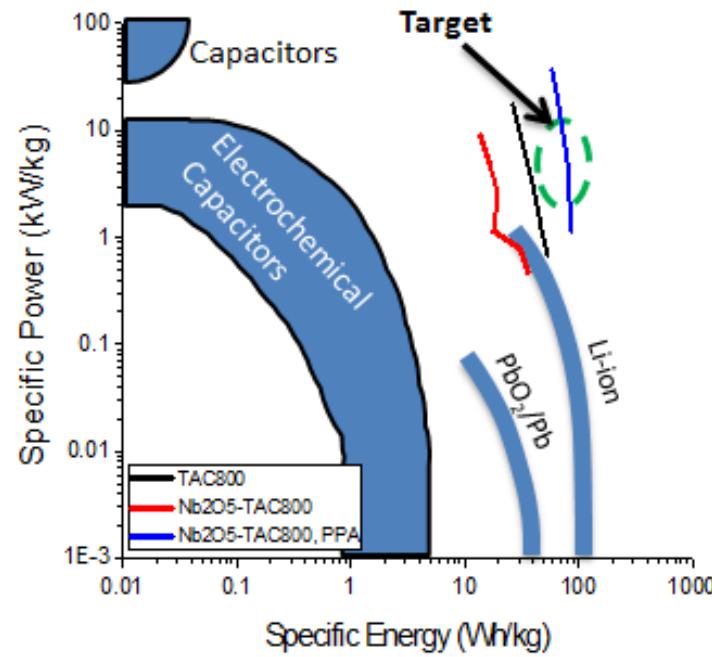
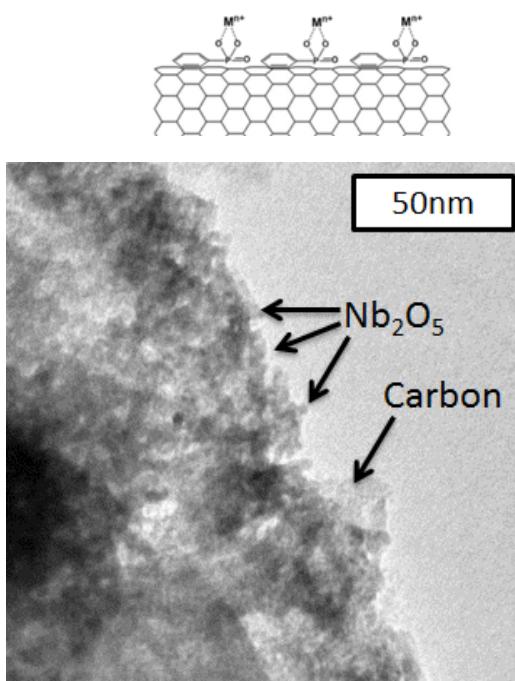
Ammonium Niobate Oxalate Hydrate, Water, Carbon, Urea, 200°C, 4 days



With PPA bonding agent

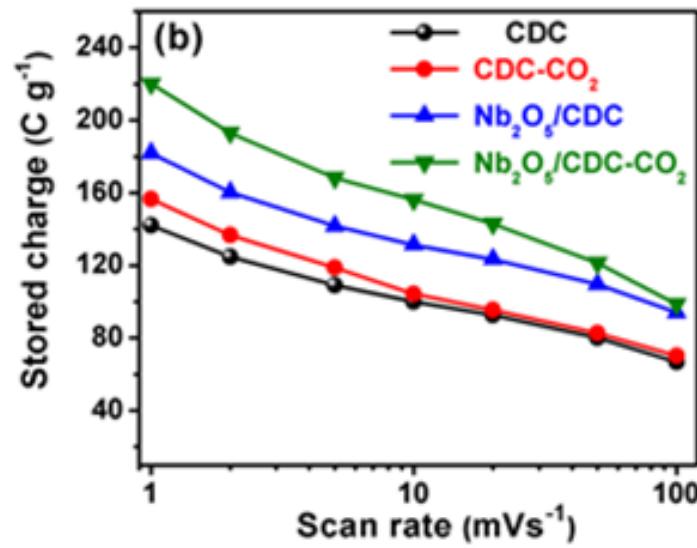
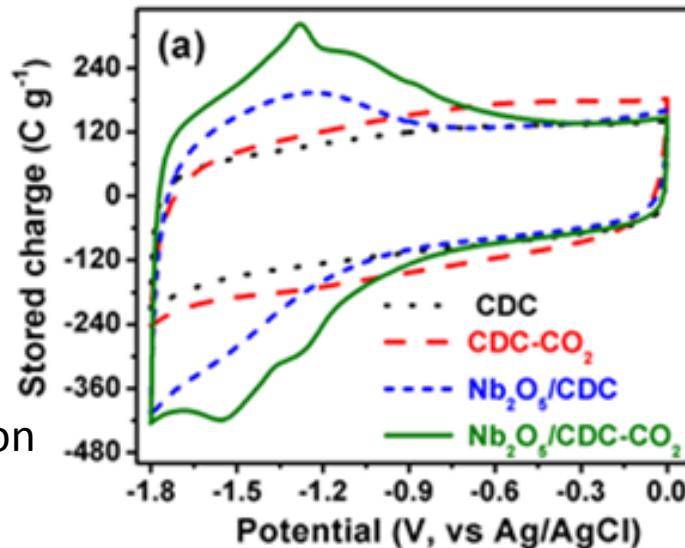
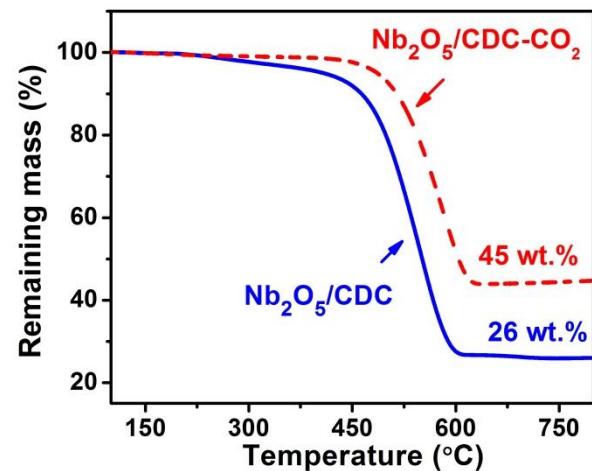
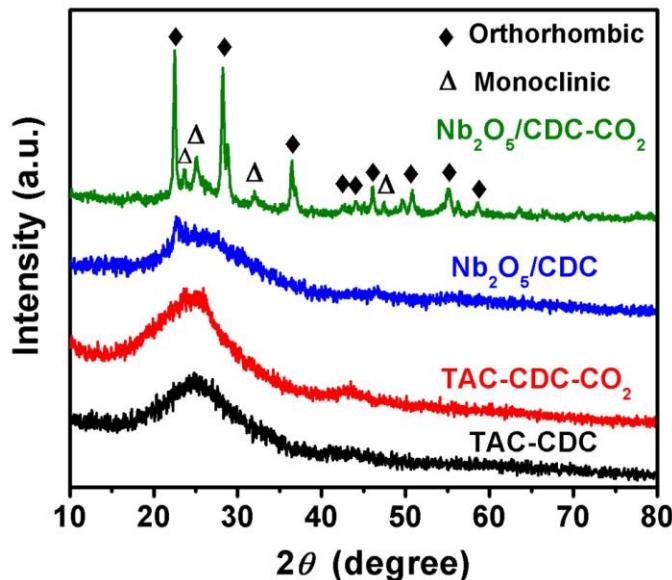
Carbon: TAC800
Metal-oxide: Nb_2O_5
Crystallinity: Amorphous
% oxide: 20%
Synthesis: Hydrothermal

Ammonium Niobate Oxalate Hydrate, Phenylphosphonic Acid, Water, Carbon, Urea 200°C, 4 days



Crystallizing the Nb_2O_5 : heat treatment in CO_2

- Temperature: 850 °C
- Time: 1 h
- CO_2 flow rate:
10 sccm
- Nb_2O_5 crystallizes and increases amount of stored charge
- Only slight oxidation of CDC



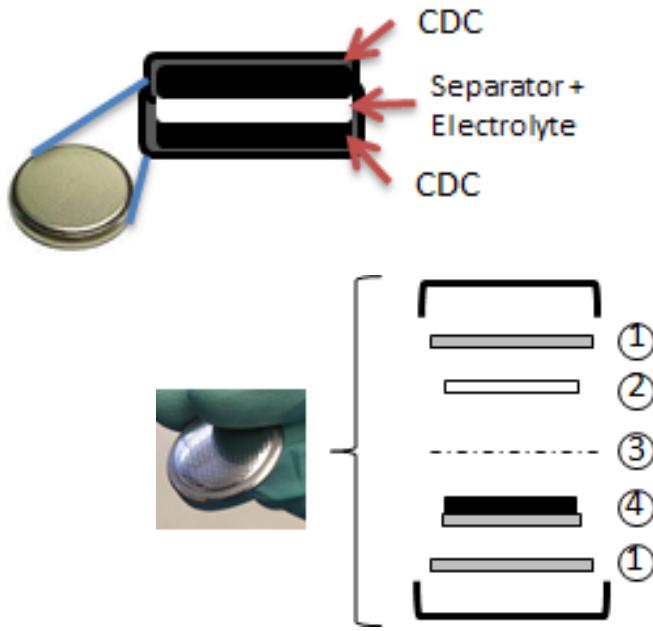
Swagelok cells

1.5 mg in weight, 5 mm
in diameter, 70 μm thick
8 : 1 : 1

$\text{Nb}_2\text{O}_5/\text{CDC}$: PTFE : carbon
7.5 mg/cm²

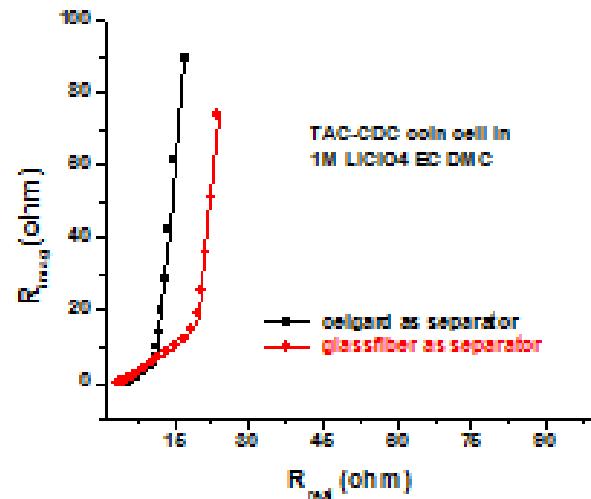
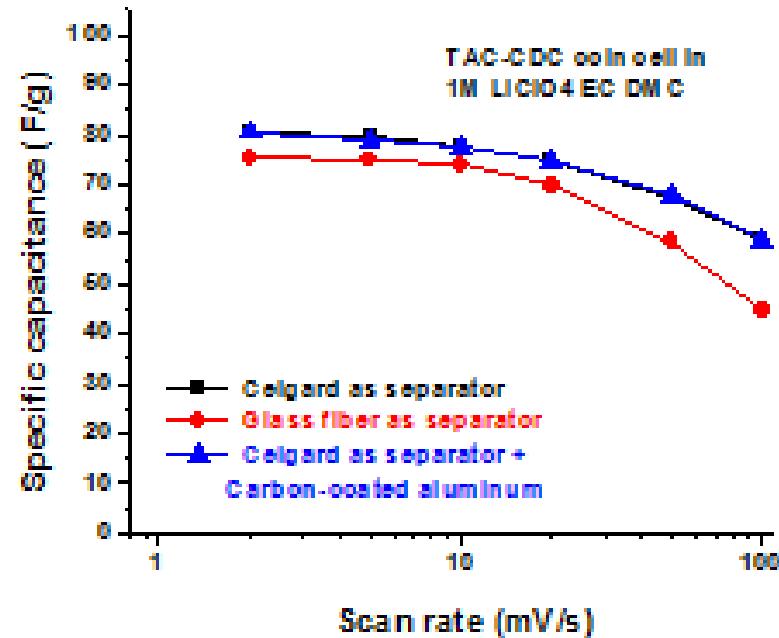
First Generation Supercapacitor: CDC electrodes with non-aqueous electrolyte

Coin Cell Devices



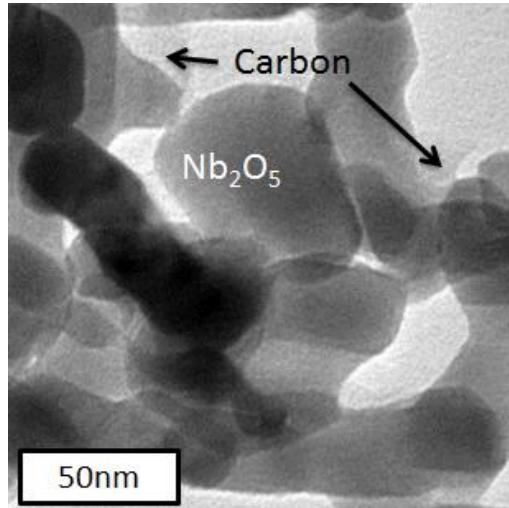
- (1) Spacer: stainless steel
- (2) CE&RE: Li
- (3) Separator
- (4) WE: active material/carbon black/PVdF

- Optimization of coin cell design parameters leads to increased specific capacitance
- $\text{Nb}_2\text{O}_5/\text{CDC-CO}_2$ composites to be substituted for CDC



New Directions for Enhanced Charge Storage: Nb_2O_5 – C Core/Shell

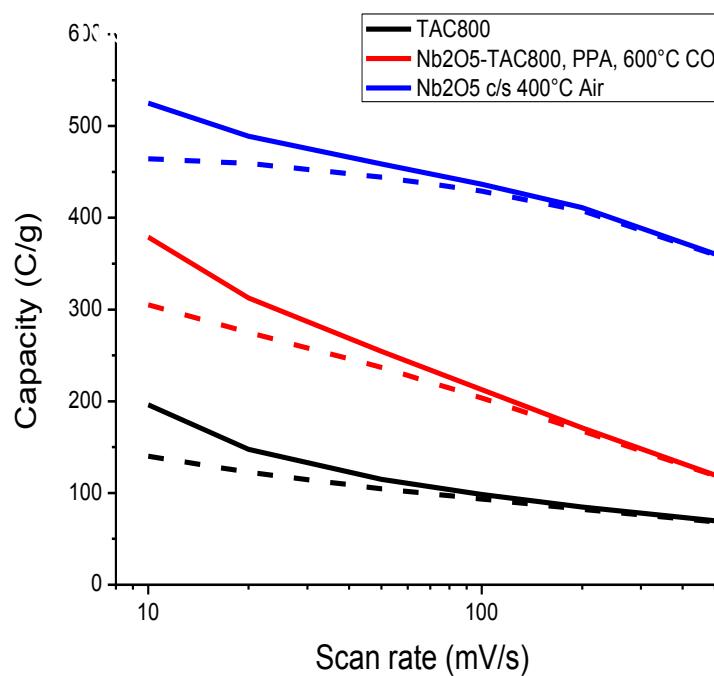
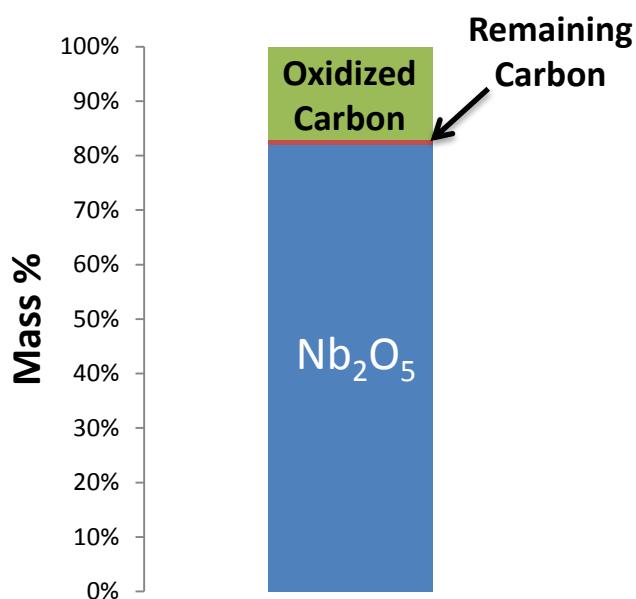
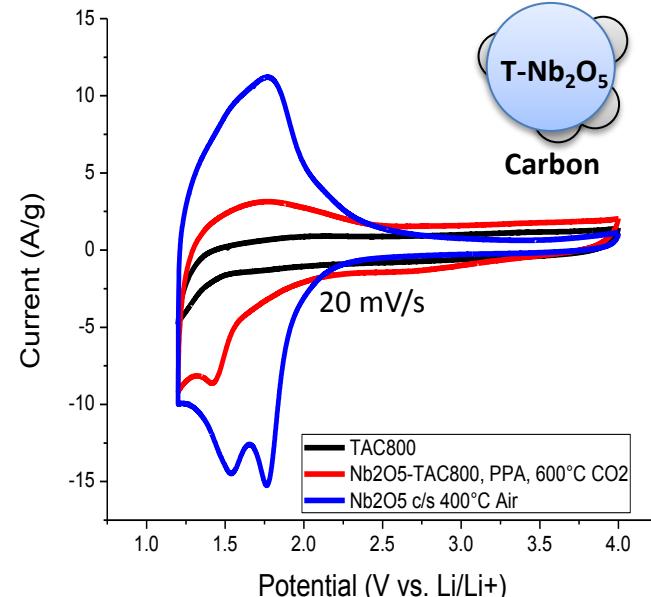
Sol-gel synthesis of Nb_2O_5 precursor gel; supercritical drying; calcine at 700°C in air; orthorhombic Nb_2O_5



Carbon shell formed by microwave hydrothermal coating of glucose

Glucose pyrolysis: 700°C in Ar

Partial oxidation: 400°C in Air



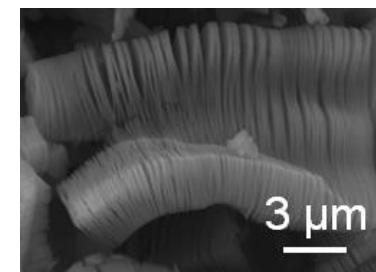
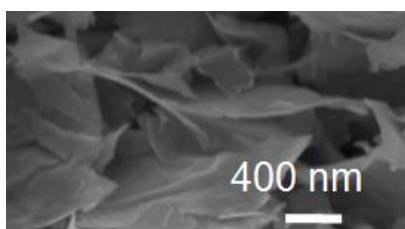
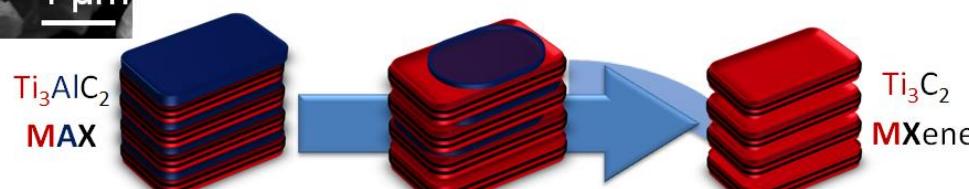
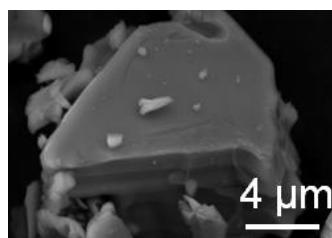
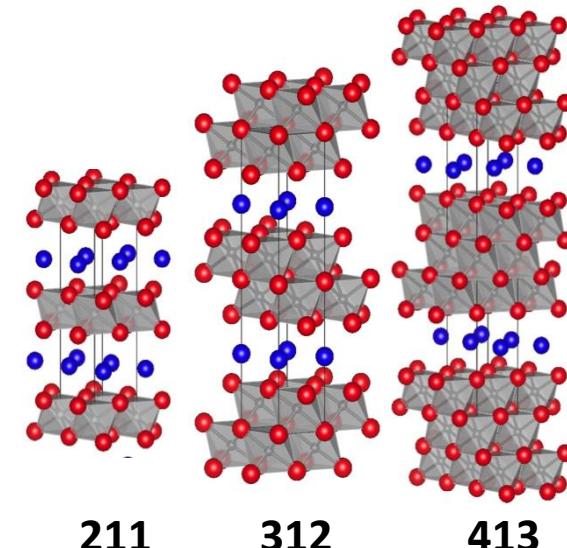
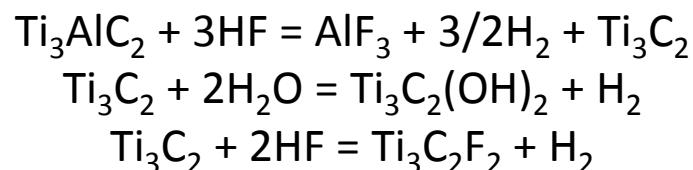
New Directions for Enhanced Charge Storage: Oxidation of Layered Nb_2C

Two-Dimensional Transition Metal Carbides, Oxycarbides and Carbonitrides

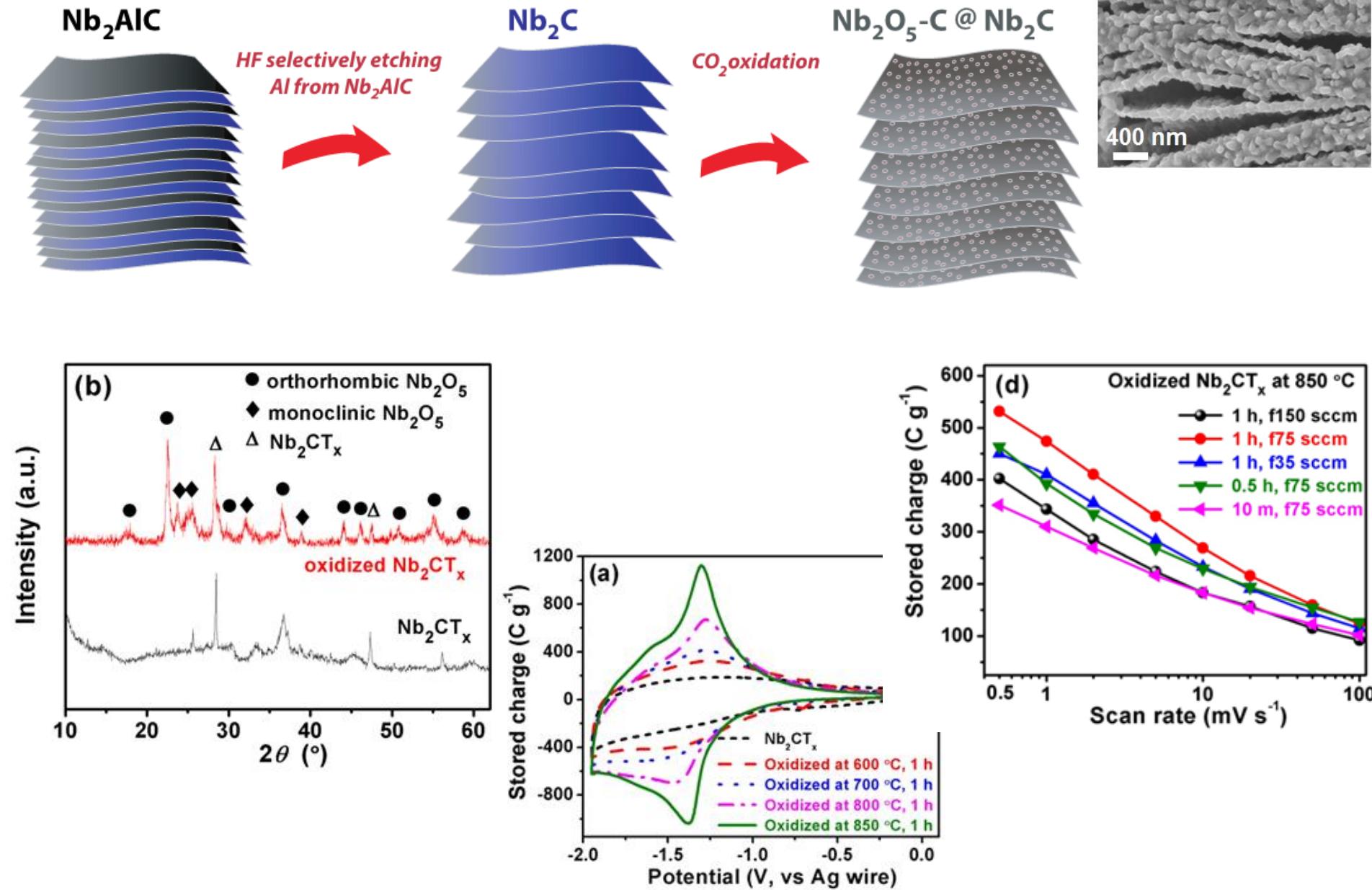
Composition of $\text{M}_{n+1}\text{AX}_n$; with $n = 1, 2, 3$; Layered hexagonal structure ($\text{P}6_3/\text{mmc}$)

Examples: Ti_2AlC , Ti_2AlN , Ti_3AlC_2 , Ti_4AlN_3 , Ta_2AlC , Ta_4AlC_3 ,
 Cr_2AlC , Cr_3AlC_2 , V_2AlC , V_3AlC_2 , **Nb₂AlC**, **Nb₄AlC₃** (>70 phases)

Delamination to Mxene
via HF treatment:



New Directions for Enhanced Charge Storage: Oxidation of Layered Nb_2C



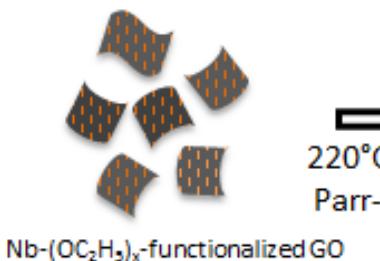
New Directions for Enhanced Charge Storage: Nb_2O_5 – RGO

- *Synthesis Route*

15 ml H_2O + 15 ml EtOH
0.96g NbCl_5
43 mg graphene oxide

Nb_2O_5 nanocrystals on
reduce graphene oxide (RGO)

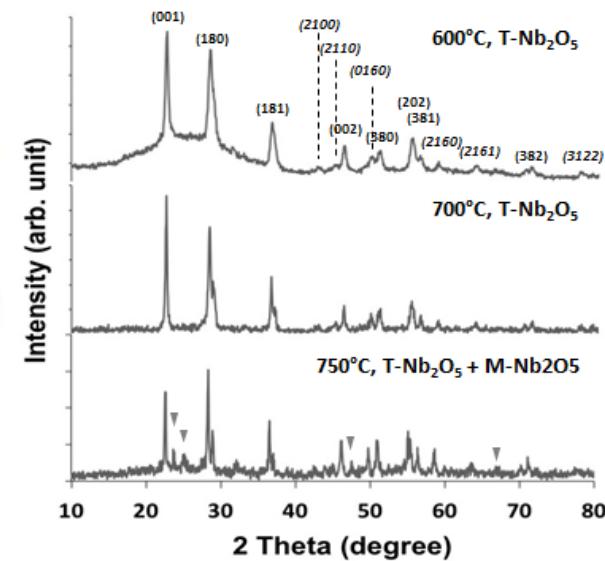
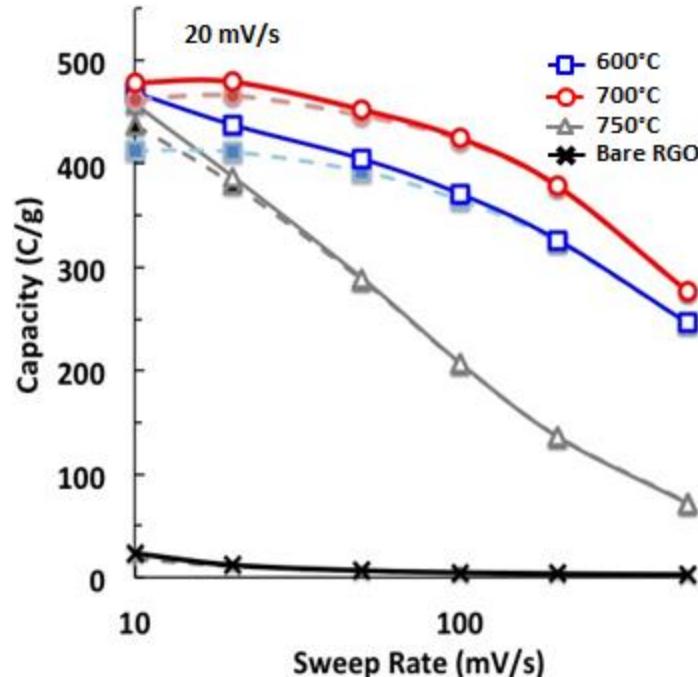
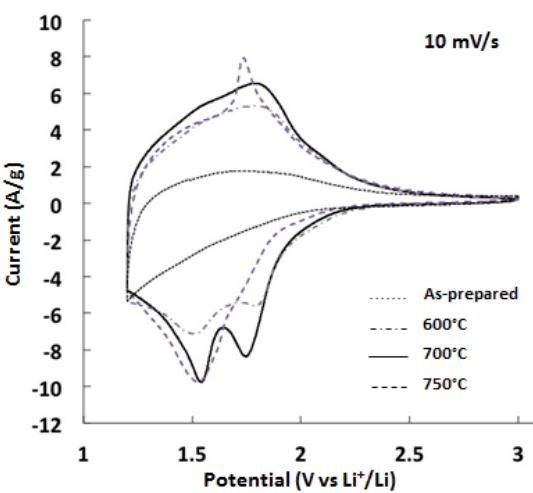
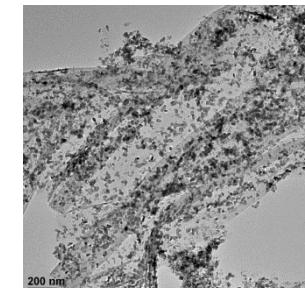
T- Nb_2O_5 /RGO
(88% oxide)



220°C-10hr
Parr-bomb



Post-annealing
700°C in Ar



Summary and Ongoing/Future Work

Progress to Date

- Generation I devices based on CDC
- Composite electrodes of $\text{Nb}_2\text{O}_5/\text{CDC-CO}_2$ demonstrate enhanced charge storage
- New approaches identified for metal oxide systems with greater storage

Ongoing and Future work

- Fabrication of coin cells incorporating $\text{Nb}_2\text{O}_5/\text{CDC-CO}_2$ electrode materials (symmetric and asymmetric)
- Development of new metal oxide/CDC electrodes
 - electrode characterization and downselect most attractive candidates
 - extend electrode studies to aqueous electrolytes and identify most promising materials

Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Electricity, Energy Storage Research Program, through Sandia National Laboratory