High Energy Density, Asymmetric Supercapacitors

Priyanka Pande, Paul Rasmussen and Levi Thompson

University of Michigan

Saemin Choi and Stefan Heinemann

Inmatech

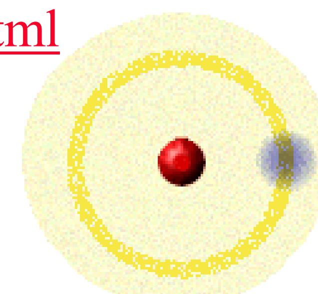
Yi Ding

TARDEC

ltt@umich.edu

www.engin.umich.edu/dept/cheme/people/thompson/ltt.html

www.hydrogen.umich.edu



Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
10 APR 2012	**Briefing Charts**	**01-01-2012 to 01-03-2012**

4. TITLE AND SUBTITLE **High Energy Density Asymmetric Supercapacitors**	5a. CONTRACT NUMBER **W56HZV-04-2-0001**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Yi Ding; Priyanka Pande; Paul Rasmussen; Levi Thompson; Saemin Choi**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **University of Michigan,Engineering Department,500 South State Street,Ann Arbor,MI,48109**	8. PERFORMING ORGANIZATION REPORT NUMBER **; #22799**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **U.S. Army TARDEC, 6501 East Eleven Mile Rd, Warren, Mi, 48397-5000**	10. SPONSOR/MONITOR'S ACRONYM(S) **TARDEC**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **#22799**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
For 45th Power Conference

14. ABSTRACT
-Explore methods to maximize properties of nitride or carbide based active materials -Develop methods for fabrication of cathodes containing high surface area nitrides or carbides, and anodes containing Mn or Ni oxides -Design and assemble asymmetric prototype cells using appropriate electrolytes -Evaluate the performance of prototype for technologically relevant load profiles.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Public Release**	**20**	

Objectives and Tasks

Objectives for the project:

- Explore methods to maximize properties of nitride or carbide based active materials;
- Develop methods for fabrication of cathodes containing high surface area nitrides or carbides, and anodes containing Mn or Ni oxides;
- Design and assemble asymmetric prototype cells using appropriate electrolytes;
- Evaluate the performance of prototype for technologically relevant load profiles.

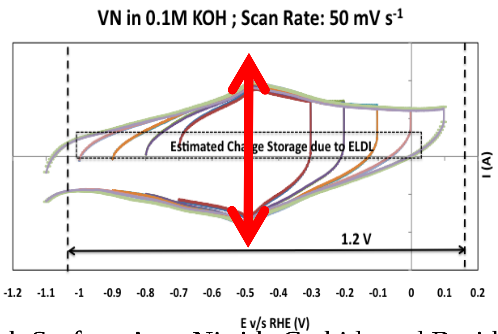
Tasks for funding cycle:

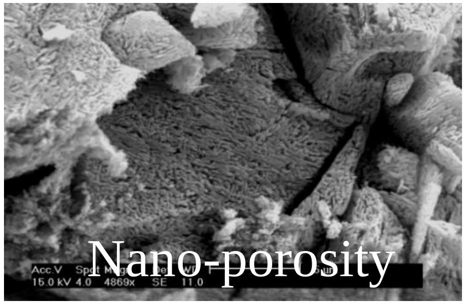
- Fabricate prototype cells incorporating nitride and oxide electrode materials;
- Characterize prototype functional properties including capacitance, energy density and coulombic efficiency;
- Characterize prototype functional properties including cycle-life and low temperature tolerance

Asymmetric Capacitor Design

- High Surface Area Electrodes → Enhanced Capacitance

$$E = \frac{CV^2}{2}$$

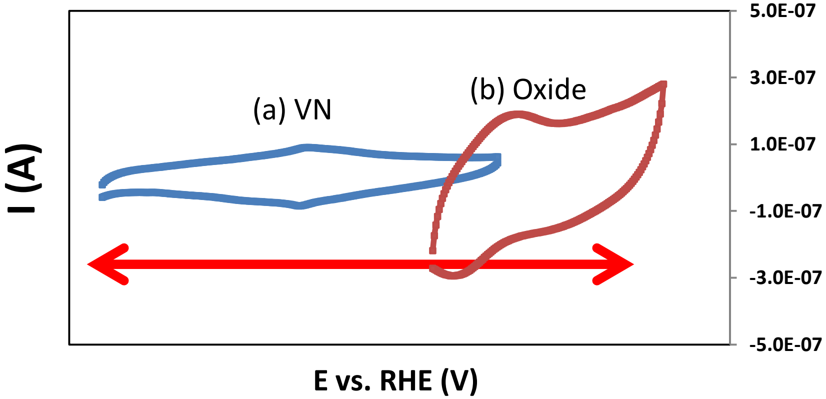




•US 5,680,292 High Surface Area Nitride Carbide and Boride Electrodes and Methods of Fabrication Thereof
•US 5,837,630 High Surface Area Mesoporous Desigel materials and Methods for Their Fabrication

- Asymmetric Design → Widened Potential Window

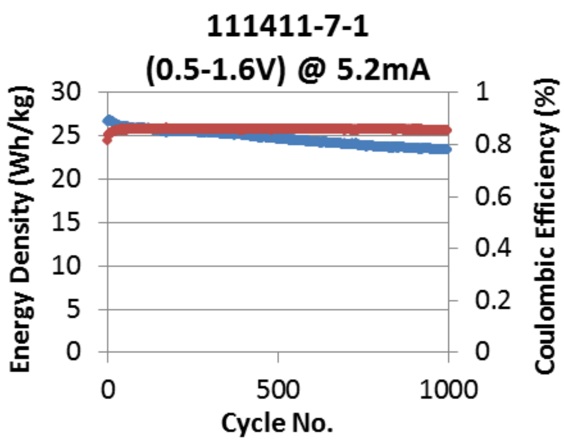
$$E = \frac{CV^2}{2}$$



•US Patent Pending High Performance Transition Metal Carbides/Nitrides based Asymmetric Capacitors

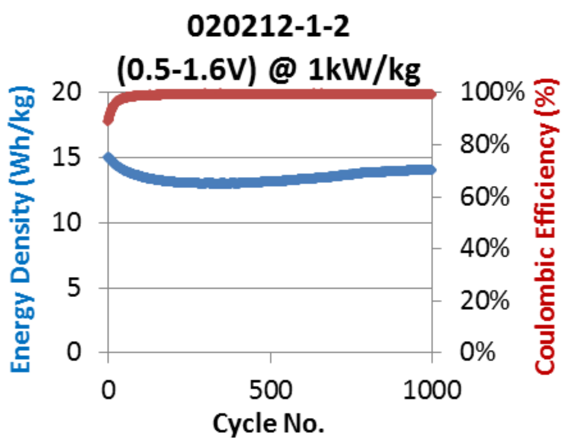
- Aqueous Electrolytes → Cheap, Non-flammable and high ionic conductivity

Asymmetric Capacitors



Cell #	NiOOH (mg)	VN (mg)	Mass Ratio	A/g	Potential (V)	Wh/kg* @1000 cycle
111411-7-1	2.6	2.6	1.0	1.0	1.6 - 0.5	23.4

* Based on active material using button cell.
1. PVDF as binder
2. Ni current collector

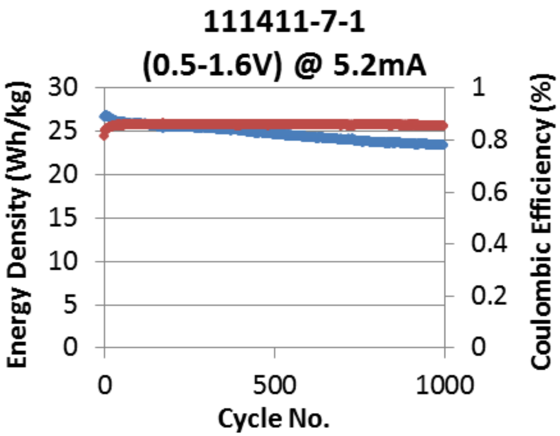


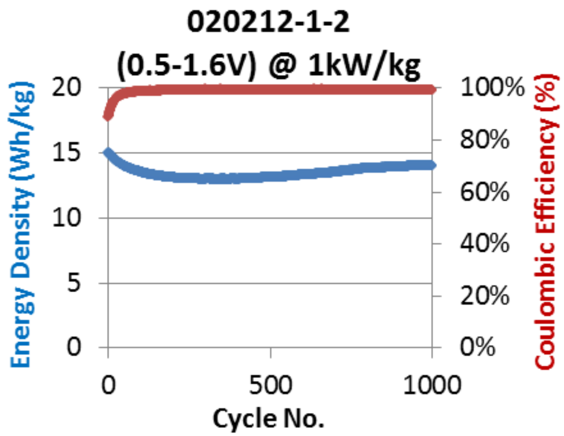
Cell #	NiOOH (mg)	VN (mg)	Mass Ratio	Potential (V)	Wh/kg* @ 1 kW/kg* & 1000 cycle
020212-1-2	69.1	65.0	1.1	0.5-1.6V	14.1

* Based on active material using button cell.
1. PTFE (Teflon) as binder
2. Ni foam current collector

Optimize components (e.g. binder, foam) and processes (e.g. mass ratio)

Asymmetric Capacitors





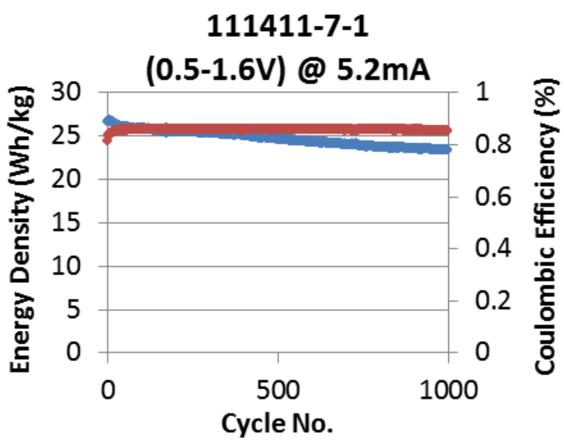
Anticipated Performance

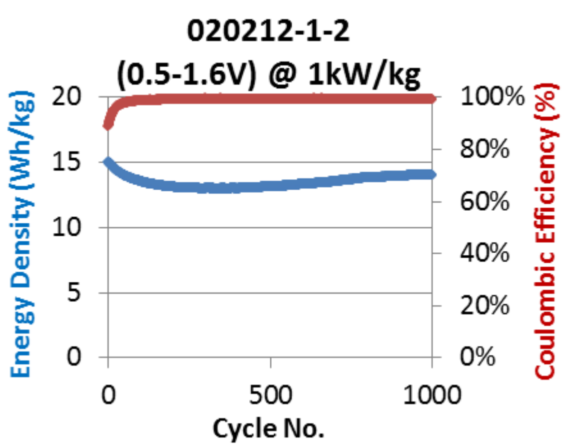
Cell Dimensions	5.1 cm x 7.6 cm x 2.1 mm
Cell Weight	22.9 g
Cell Volume	7.8 ml
Total Active Material	7.9 g
# of Electrode Pairs	3
Total Energy	0.1 Wh
Gravimetric Energy*	4.8 Wh/kg
Volumetric Energy*	14.2 Wh/L
Packaging Efficiency	35%
Peak Power	1728 W/kg

* Power density of 1 kW/kg (per active material)

Optimize components (e.g. binder, foam) and processes (e.g. mass ratio)

Asymmetric Capacitors





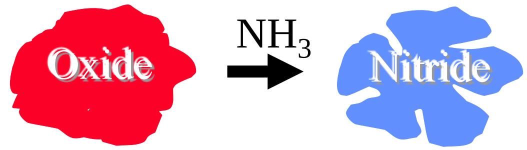
Optimize components (e.g. binder, foam) and processes (e.g. mass ratio)

VN Synthesis

- High surface area nitrides and carbides
  - Pseudomorphic reactions

    Volpe and Boudart, 1985

<2 m^2/g

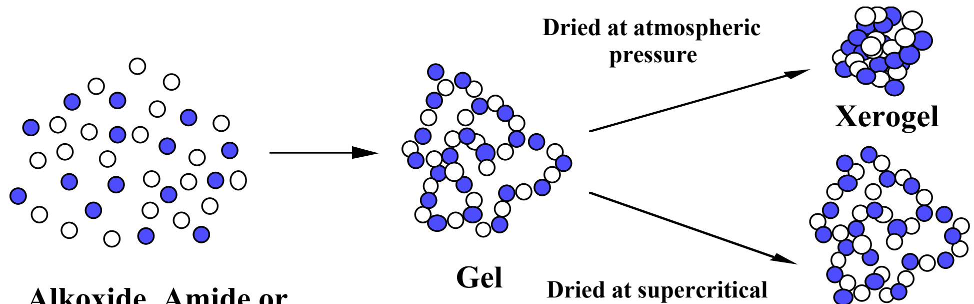


>100 m^2/g

$\rho_{MoO3} = 4.7\ g/cm^3$ $\rho_{Mo2N} = 9.4\ g/cm^3$

- Solution Chemical Methods
  - Sol-gel synthesis

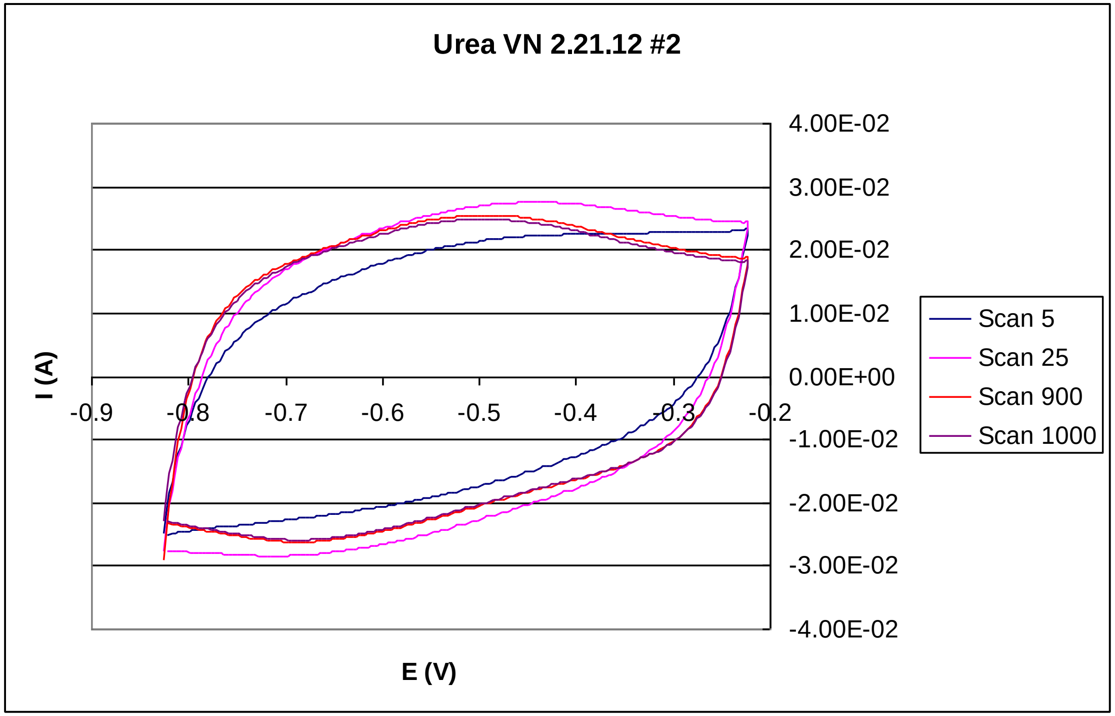
    Thompson et al, 1998



  - Urea method
    - Ethanol, vanadium oxy-trichloride ($VOCl_3$) and urea
    - Age for 12-18 hr
    - Heat to 800 °C @ 3 C/min for 3 hours under flowing N_2

Synthesis of VN

- Surface area: 222 m^2/g
- Capacitance: 239 F/g



1M potassium hydroxide
Hg/HgO reference electrode
Platinum counter electrode
50 mV/s

Charge Storage Mechanism

Material	Stability Window (V)	Capacitance (F/g)	Surface Area (m^2/g)
VN	1.1 (KOH)	210	38
VC	0.8 (KOH)	2.6	6
Mo_2N	0.8 (H_2SO_4)	346	152
W_2C	0.7 (H_2SO_4)	79	16
W_2N	0.8 (KOH)	25	42

- Double-layer capacitance typically ~25 μF/cm^2 (0.25 F/m^2)

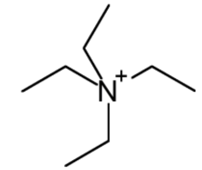
[1]Conway B E; *Electrochemical Supercapacitors;* (1999).

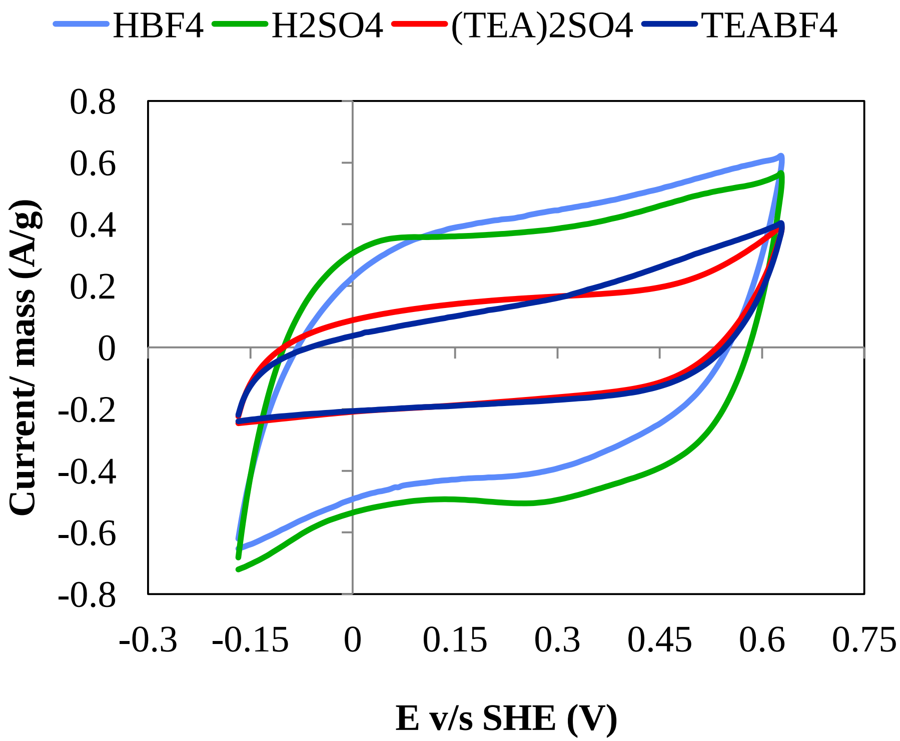
Storage Mechanism: Ion Isolation

Mo_2N

ANION / CATION	$(SO_4)^{2-}$	$(BF_4)^-$
H^+	H_2SO_4 pH: 1.3 0.1M	HBF_4 pH: 1.3 0.1M
$(C_2H_5)_4N^+$	$(TEA)_2SO_4$ pH: 4.9 0.1M	TEA-BF_4 pH: 4.2 0.3M

Tetraethylammonium$^+$





Constant ionic strength/ pH
Scan rate: 2 mV/s

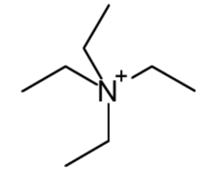
Pande et al., JECS (2011)

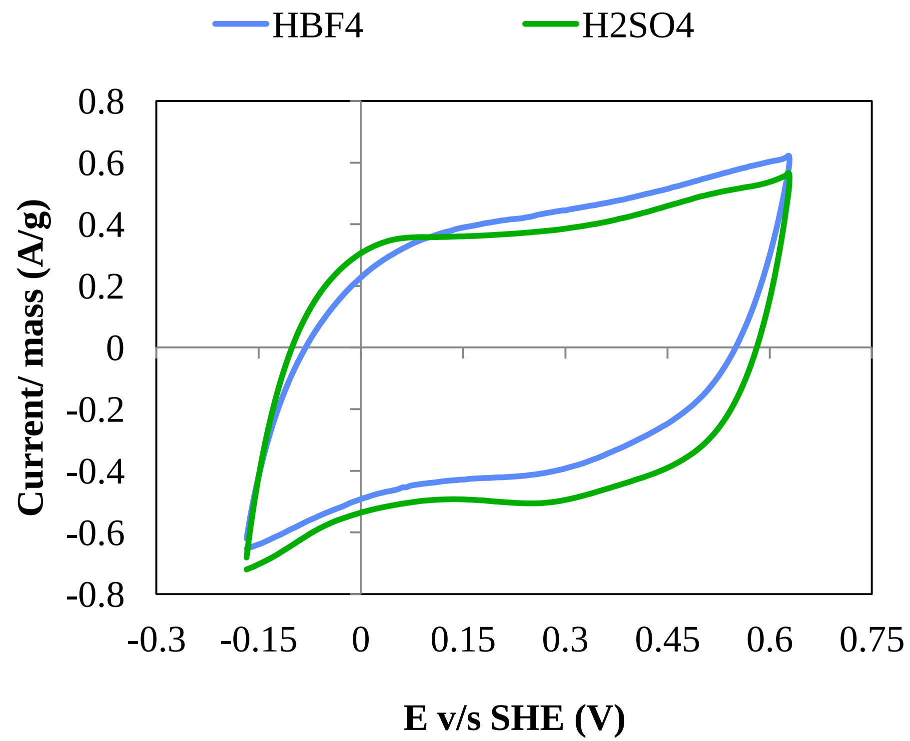
Storage Mechanism: Ion Isolation

Mo_2N

ANION / CATION	$(SO_4)^{2-}$	$(BF_4)^-$
H^+	H_2SO_4 pH: 1.3 0.1M	HBF_4 pH: 1.3 0.1M
$(C_2H_5)_4N^+$	$(TEA)_2SO_4$ pH: 4.9 0.1M	TEA-BF_4 pH: 4.2 0.3M

Tetraethylammonium$^+$





Constant ionic strength/ pH
Scan rate: 2 mV/s

Pande et al., JECS (2011)

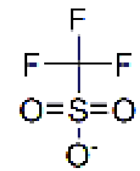
UNCLASSIFIED

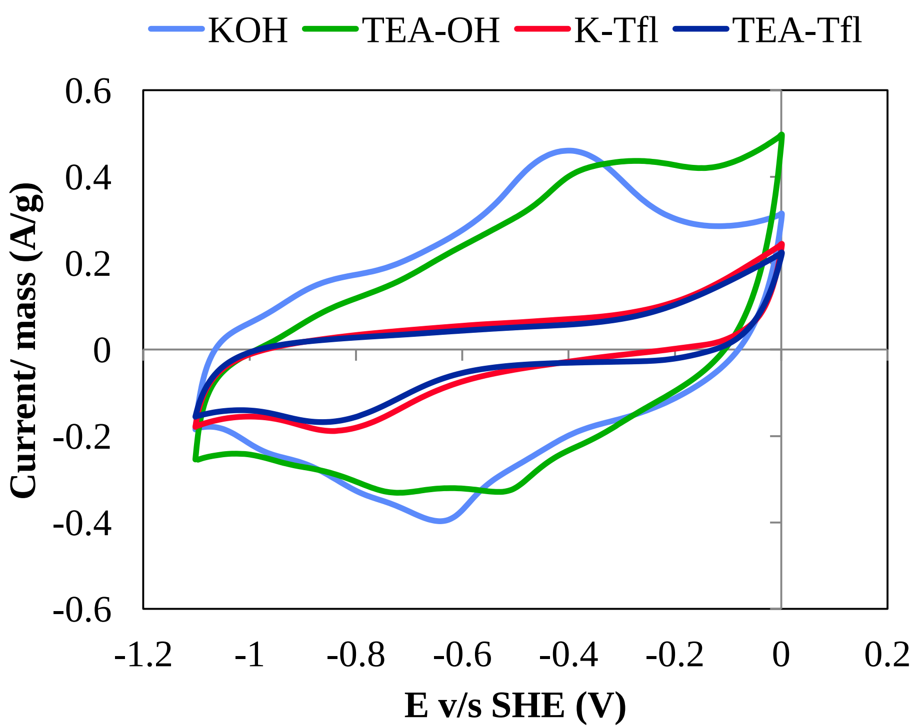
Storage Mechanism: Ion Isolation

VN

ANION / CATION	$(OH)^-$	$(CF_3SO_3)^-$
K^+	KOH pH: 12.8 0.1M	K-Tfl pH: 9.3 0.1M
$(C_2H_5)_4N^+$	TEAOH pH: 12.9 0.1M	TEA-Tfl pH: 8.1 0.1M

Triflate$^-$





Constant ionic strength/ pH
Scan rate: 2 mV/s

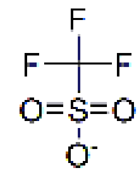
Pande et al., JECS (2011)

Storage Mechanism: Ion Isolation

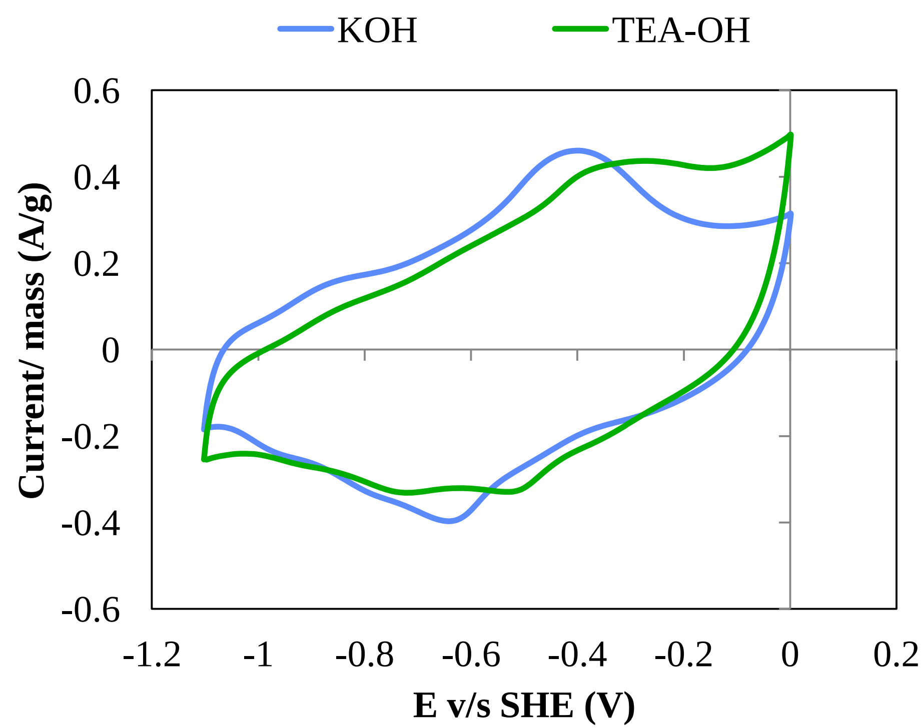
VN

ANION / CATION	$(OH)^-$	$(CF_3SO_3)^-$
K^+	KOH pH: 12.8 0.1M	K-Tfl pH: 9.3 0.1M
$(C_2H_5)_4N^+$	TEAOH pH: 12.9 0.1M	TEA-Tfl pH: 8.1 0.1M

Triflate$^-$

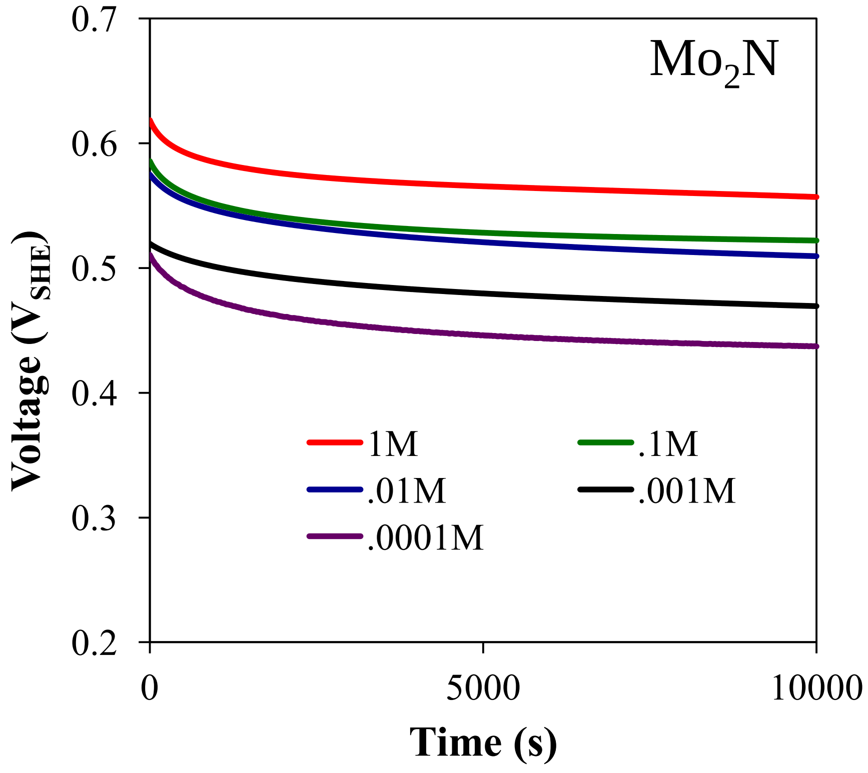


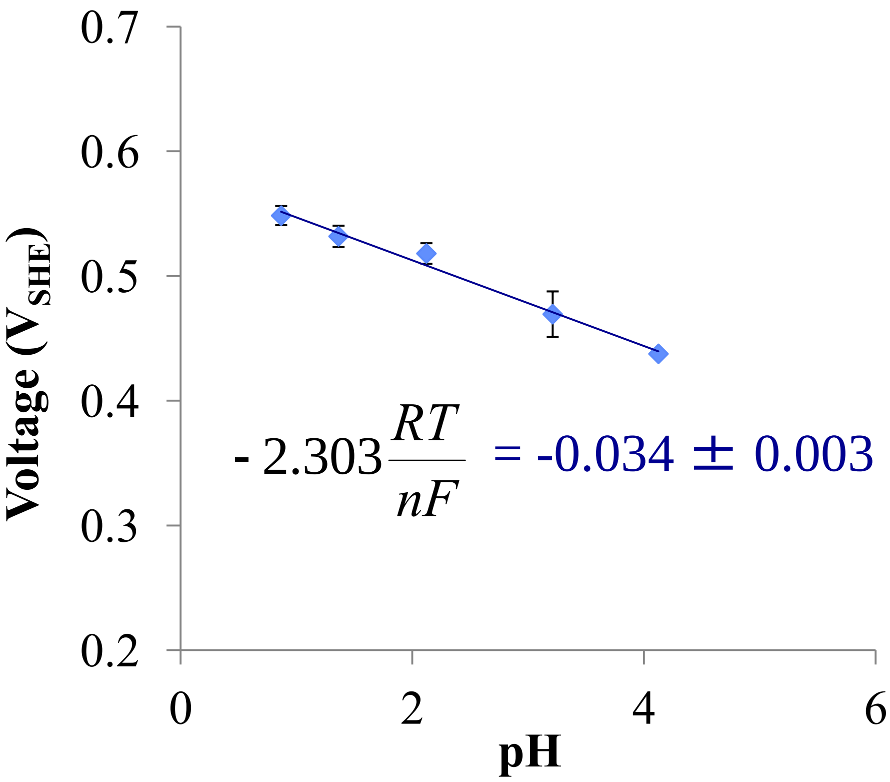
Constant ionic strength/ pH
Scan rate: 2 mV/s



Pande et al., JECS (2011)

Storage Mechanism: Charge Transfer

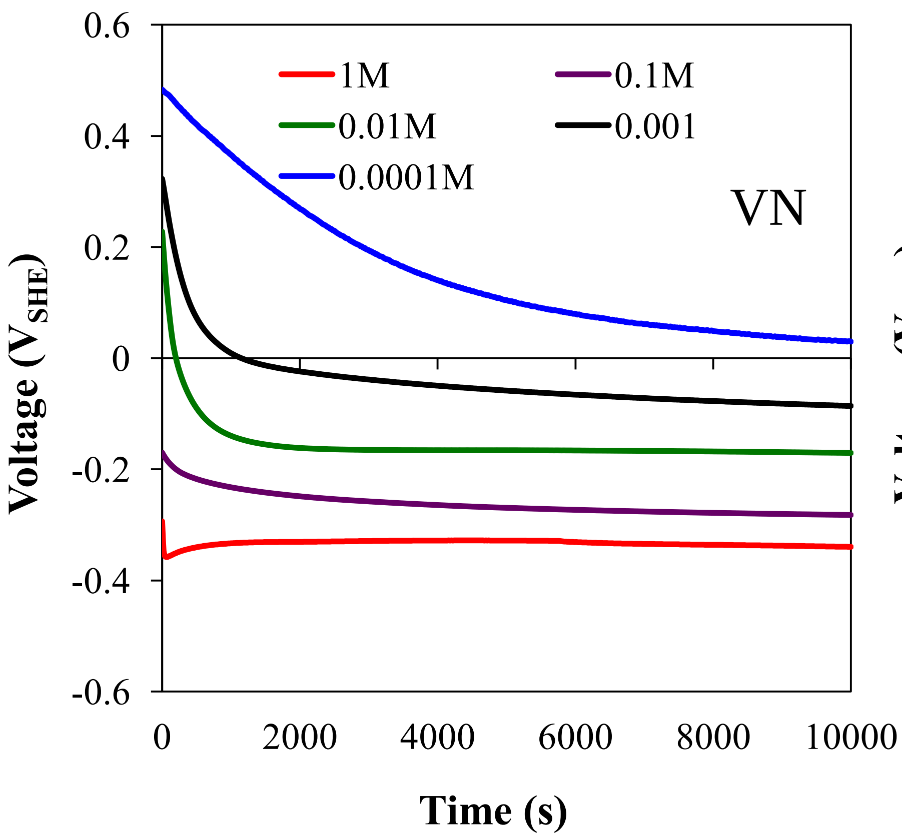


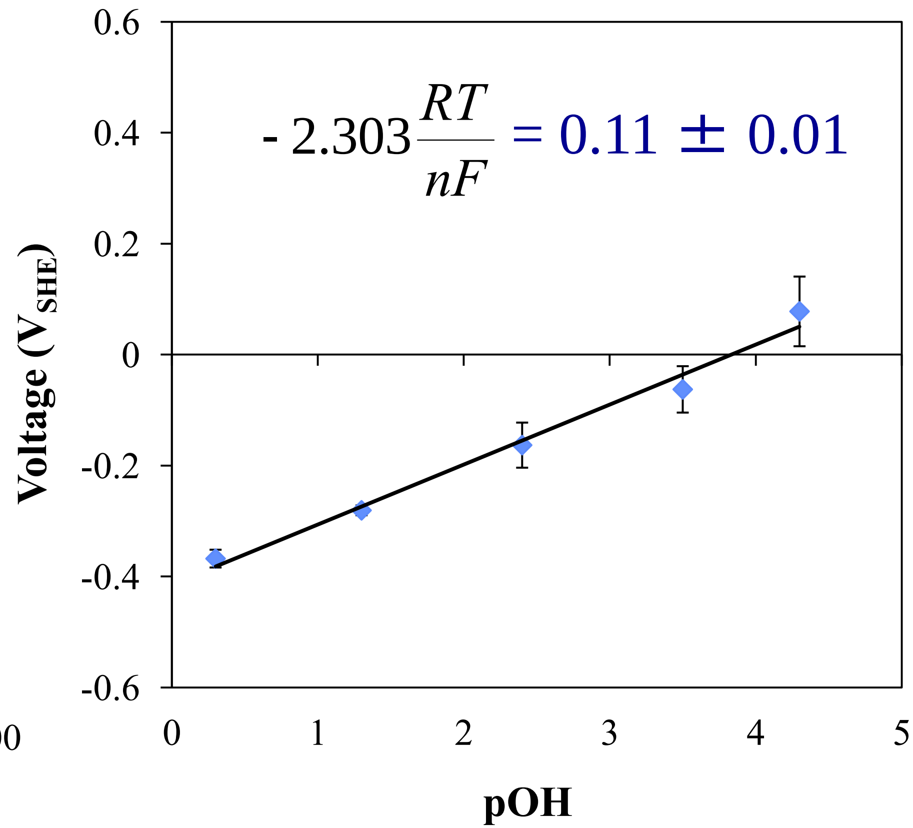


$$n = 1.7 \pm 0.2 \longrightarrow 1.5$$

$$2[(Mo^{1.5+})_2N^{3-}] + 2H^+ + 3e^- \leftrightarrow 2[(Mo^{1+})_2N^{3-}H]$$

Storage Mechanism: Charge Transfer

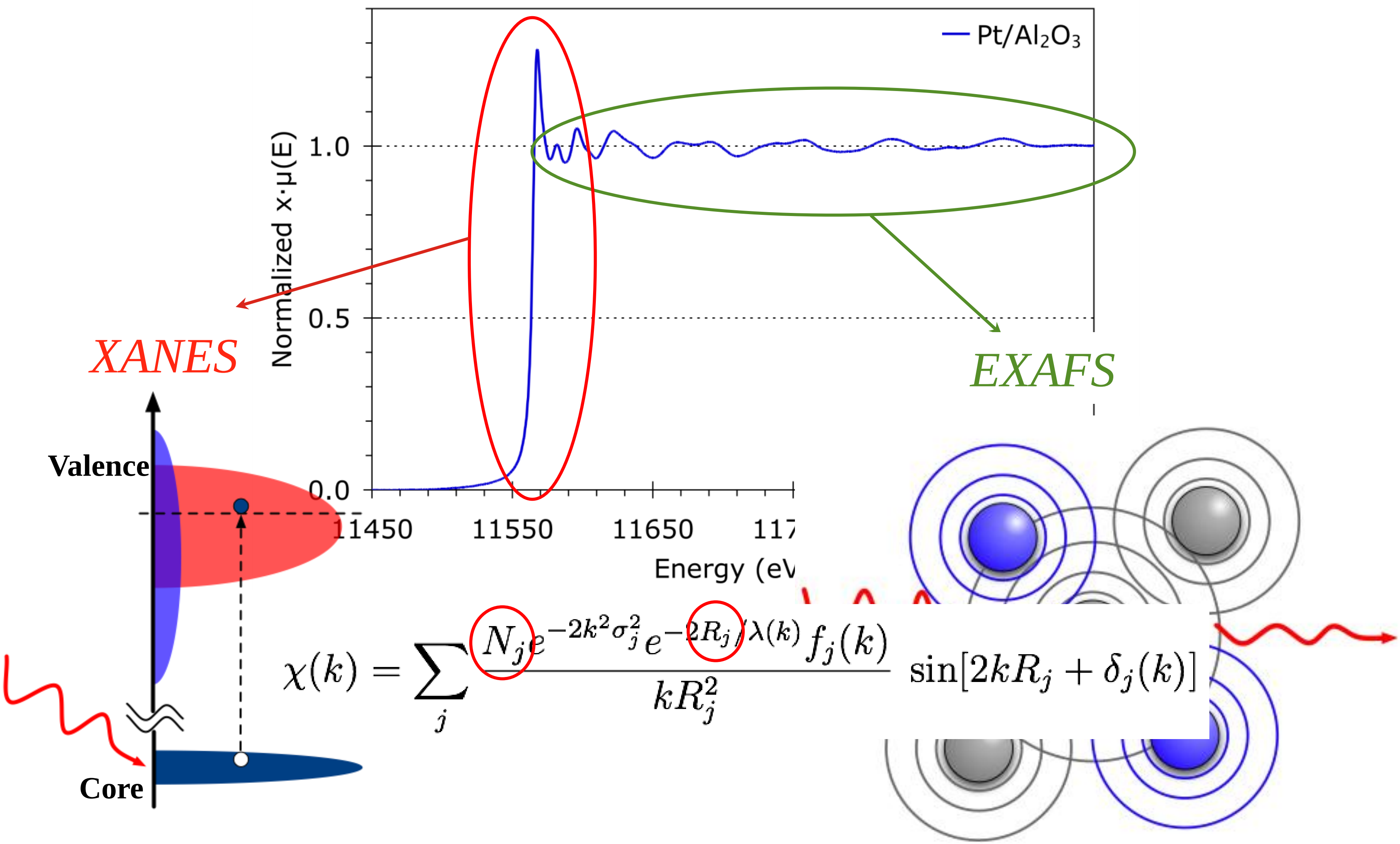




$$n = 0.54 \pm 0.08 \longrightarrow 0.5$$

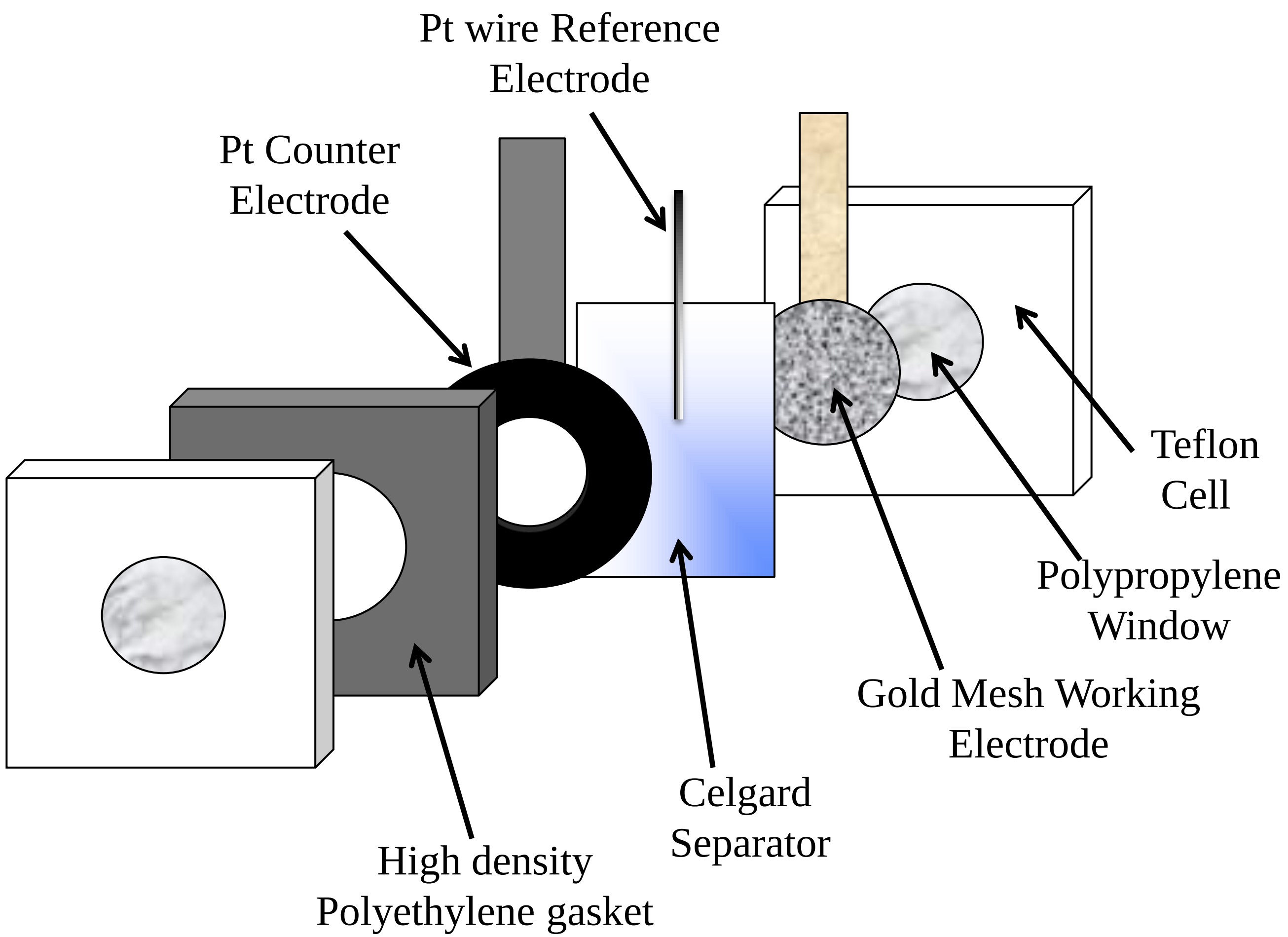
$$V^{3+}N^{3-} + 2OH^{-} \leftrightarrow V^{2+}N^{3-}(OH)_2 + e^{-}$$

Structure-Function: X-Ray Absorption



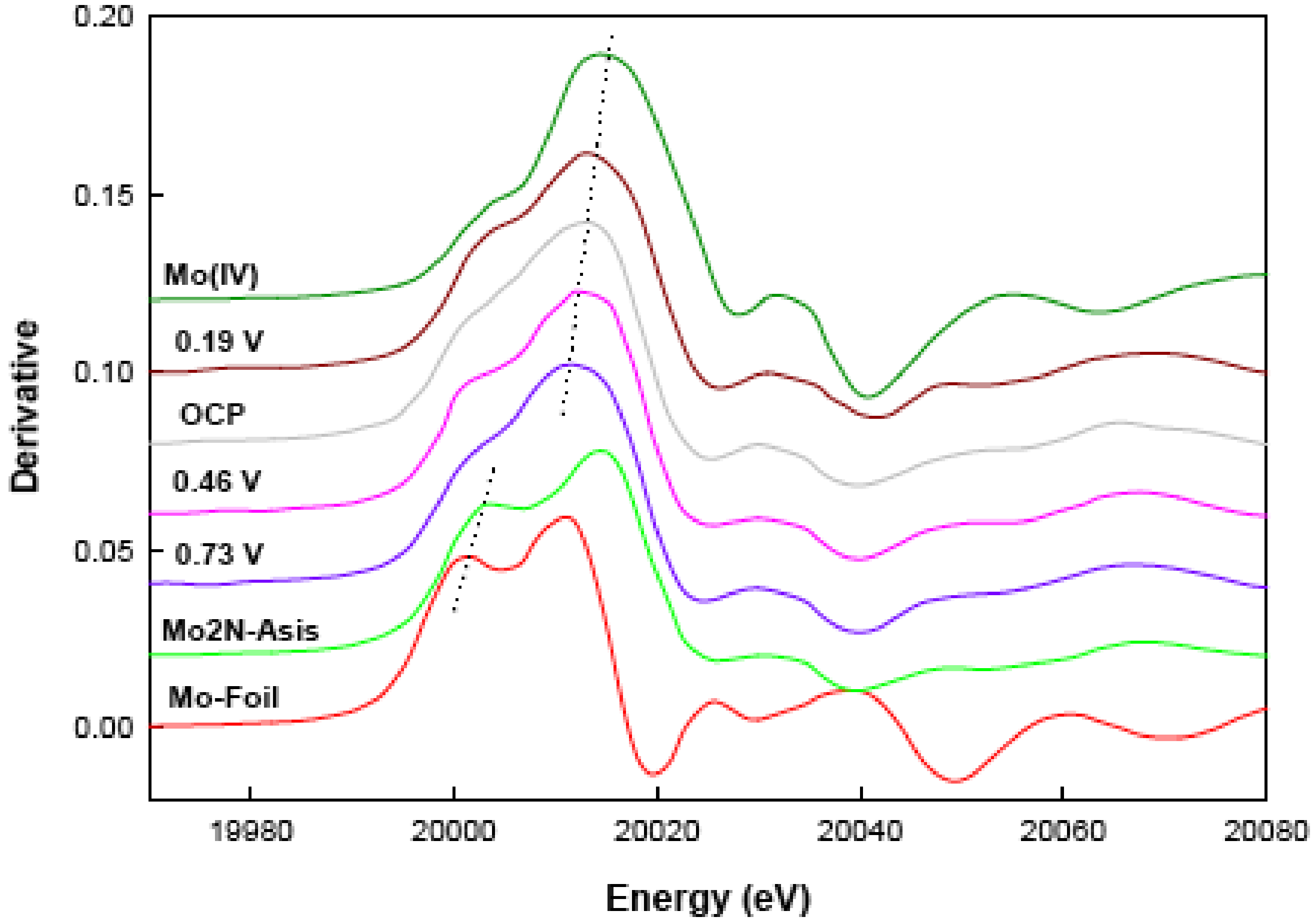
$$\chi(k) = \sum_j \frac{N_j e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} f_j(k)}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

Structure-Function: X-Ray Absorption



Structure-Function: X-Ray Absorption

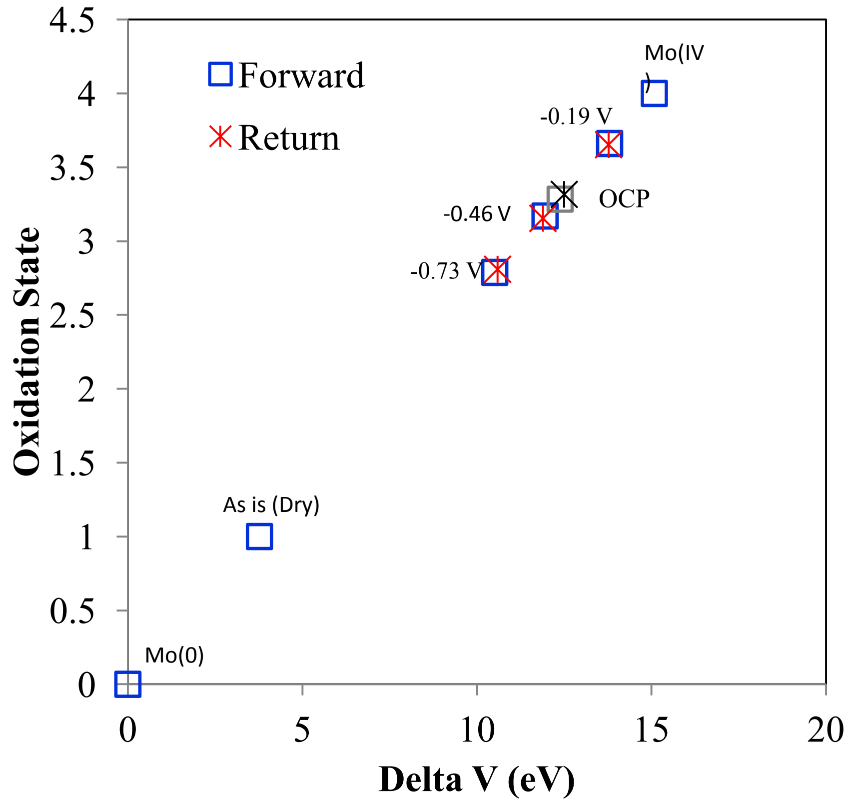
Mo_2N

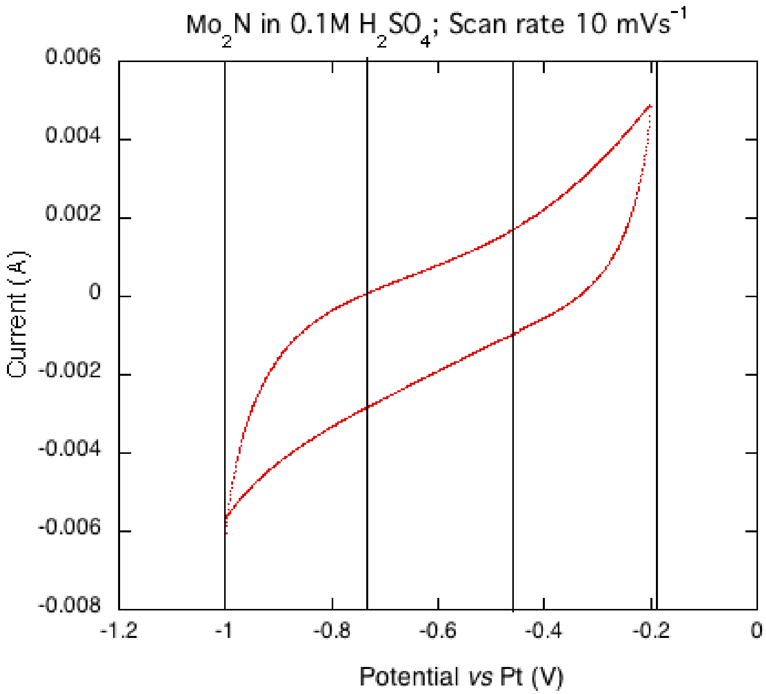


0.1M H_2SO_4
Voltage *vs* Pt reference

Structure-Function: X-Ray Absorption

Mo_2N





$Mo^{2.33+} \rightarrow Mo^{2.8+} \rightarrow Mo^{3.15+} \rightarrow Mo^{3.6+}$

0.1M H_2SO_4
Voltage *vs* Pt reference

Summary

Tasks for funding cycle:

- Fabricate prototype cells incorporating nitride and oxide electrode materials
  - Synthesized VN and oxides for use in supercapacitors
  - Assembled cells using Ni foil with >23 Wh/kg
  - Assembled cells using Ni foams with >14 Wh/kg
  - Demonstrated solution chemical method for production of high surface area VN
- Characterize prototype functional properties including capacitance, energy density and coulombic efficiency;
- Characterize prototype functional properties including cycle-life and low temperature tolerance

- Characterize charge storage mechanisms for VN and Mo_2N
  - Determined active species
  - Observed redox of metals in VN and Mo_2N