

# Electrode processes associated with the electrolytic production of Ni from molten oxides

**Bing Li**

Department of Materials Science and Engineering, MIT



3rd Reactive Metals Workshop,  
MIT , Cambridge, MA, USA  
March 3, 2007

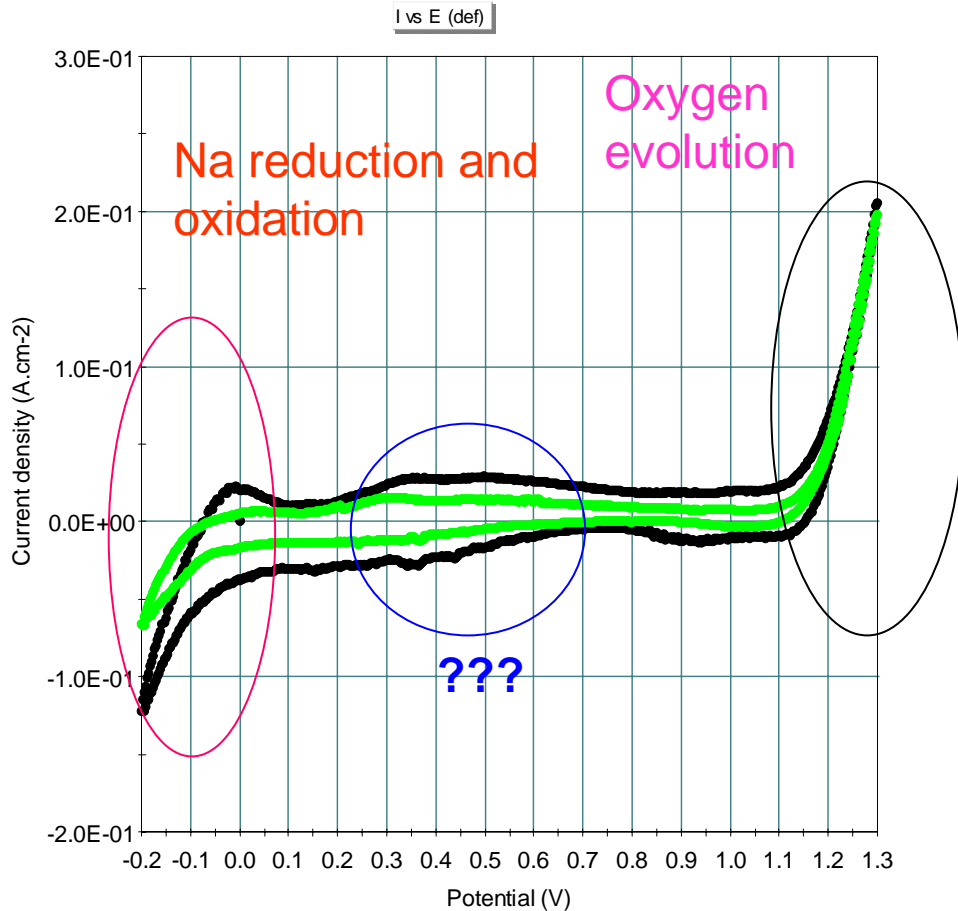
# Purpose of research

- **Professor Sadoway** has proposed producing liquid Fe and further stainless steel by **MOE (Sadoway MIT Process)**.
- We are trying to find the possibility of co-reduction of Fe, Ni and Cr from their oxides by **MOE**.
- “low-temperature” electrochemical measurements necessary of Ni redox will provide useful guidance for high-temperature efforts to produce liquid stainless steel.

# Experimental setup

- Three electrode system has been applied.
- working electrode is Pt shielded by BN, counter electrode is Pt plate.
- reference electrode is  $\text{Fe}^{2+}/\text{Fe}$  separate BN chamber
- Electrochemical data were measured by Parstat 2273.

# Supporting electrolyte CV



Electrolyte composition:

Na<sub>2</sub>O , B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>

WE: Pt (0.12cm<sup>2</sup>)

Standard decomposition potential

(at 850°C)

Na<sub>2</sub>O=2Na+0.5O<sub>2</sub> (g) -1.37V

B<sub>2</sub>O<sub>3</sub>=2B+1.5O<sub>2</sub> (g) -1.72V

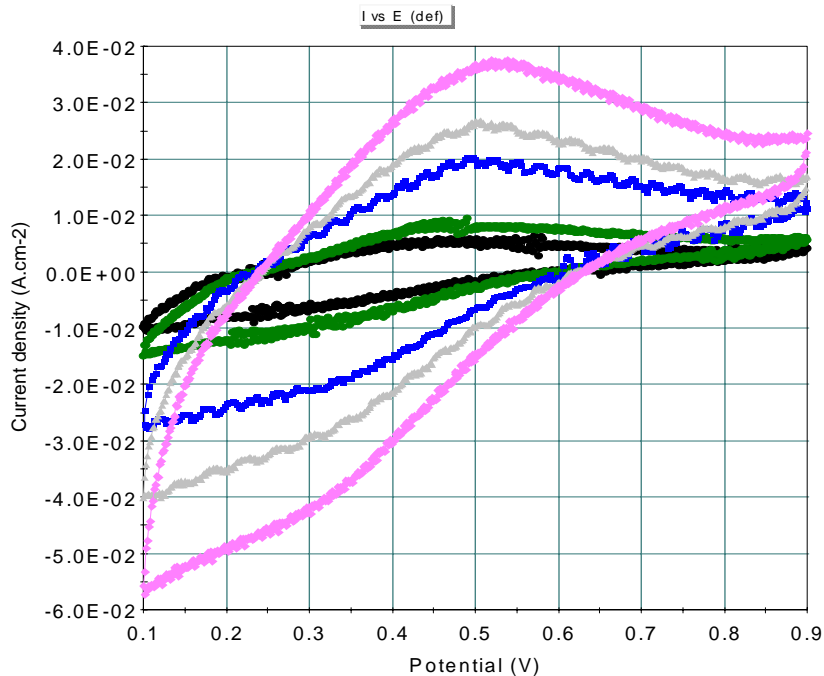
SiO<sub>2</sub>=Si+O<sub>2</sub> (g) -1.84V

NiO=Ni +0.5O<sub>2</sub> (g) -0.71V

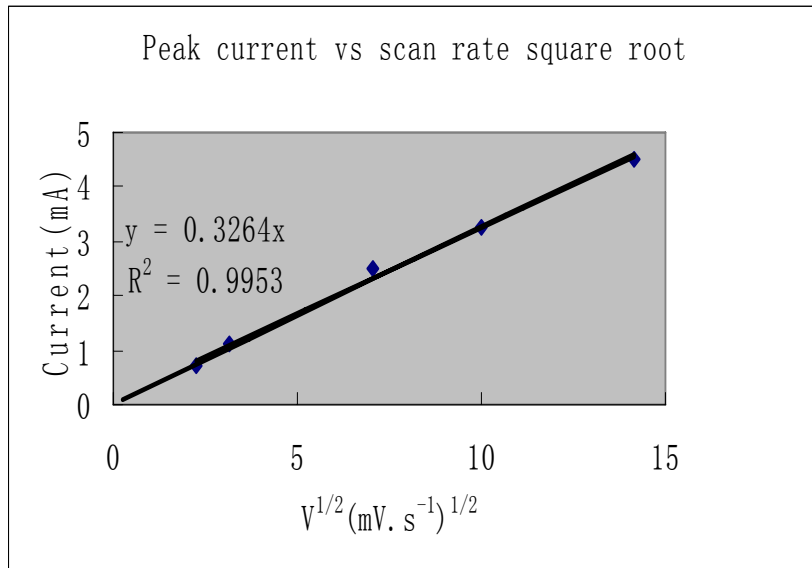
FeO=Fe+0.5O<sub>2</sub> (g) -0.99V

Scan rate (mV/s):

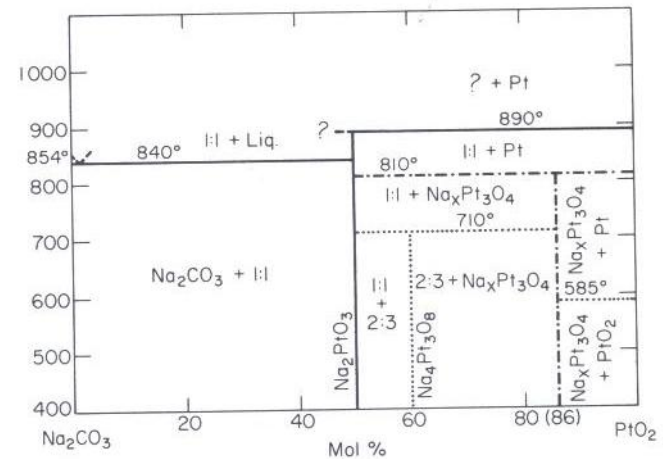
Green line : 5, Black line: 50



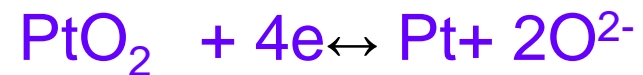
Scan rate (mV/s): Black line: 5  
 Green line: 25, Blue line: 50  
 Light gray line: 100, Pink line: 200



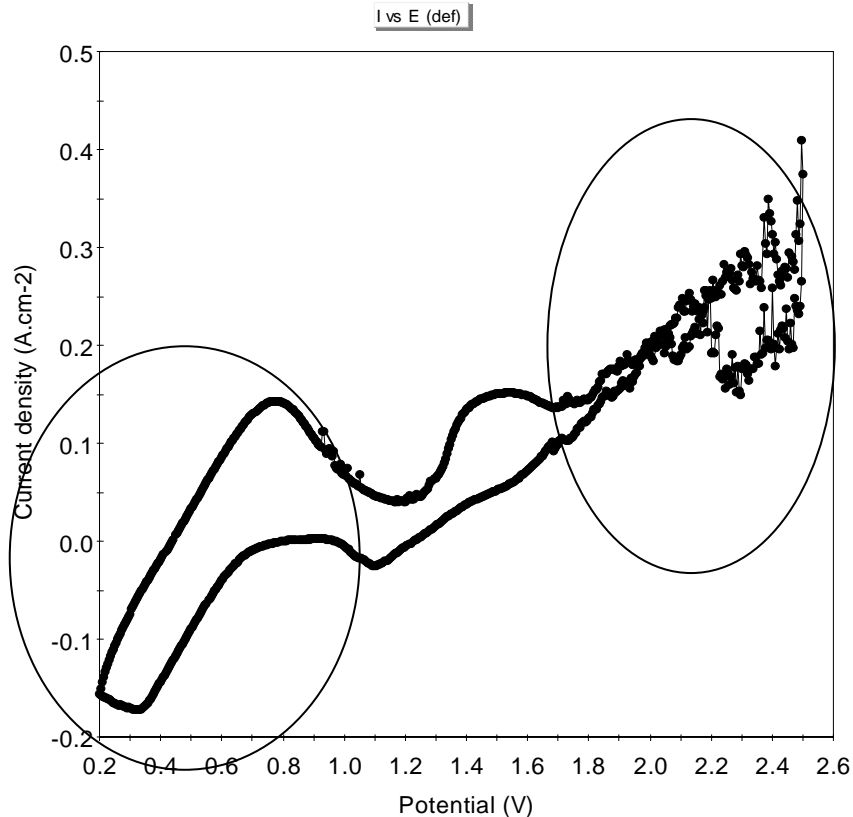
### Na-Pt-O



The electrode process is quasi-reversible. we speculate that the peaks are related to



# CV for electrolyte containing NiO



Scan rate: 50mV/s

Electrolyte composition

$\text{Na}_2\text{O} + \text{B}_2\text{O}_3 + \text{SiO}_2 + \text{NiO}$

WE: Pt shielded by BN

CE: Pt plate

RE: Fe<sup>2+</sup>/Fe separate BN chamber

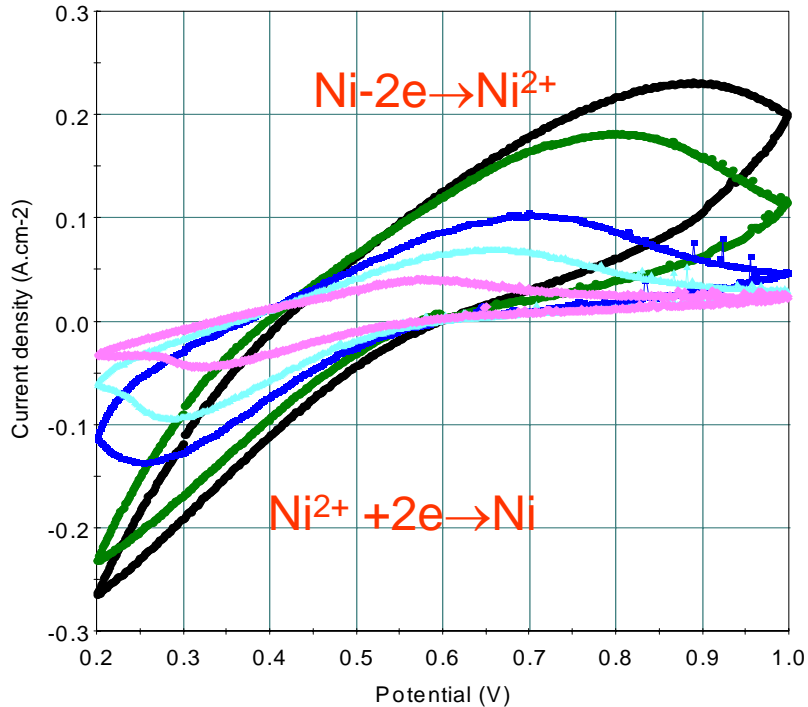
T: 850°C

standard decomposition potential  
at 850°C

$\text{NiO} = \text{Ni} + 0.5\text{O}_2(\text{g}) : -0.71 \text{ V}$

$\text{FeO} = \text{Fe} + 0.5\text{O}_2(\text{g}) : -0.99 \text{ V}$

# Ni deposition and stripping



Scan rate: mV/s

Pink line: 10

Light blue line: 50

Blue line: 100

Green line: 300

Black line: 500

standard decomposition potential  
at 850°C

$\text{NiO} = \text{Ni} + 0.5\text{O}_2 (\text{g}) : -0.71 \text{ V}$

$\text{FeO} = \text{Fe} + 0.5\text{O}_2 (\text{g}) -0.99 \text{ V}$

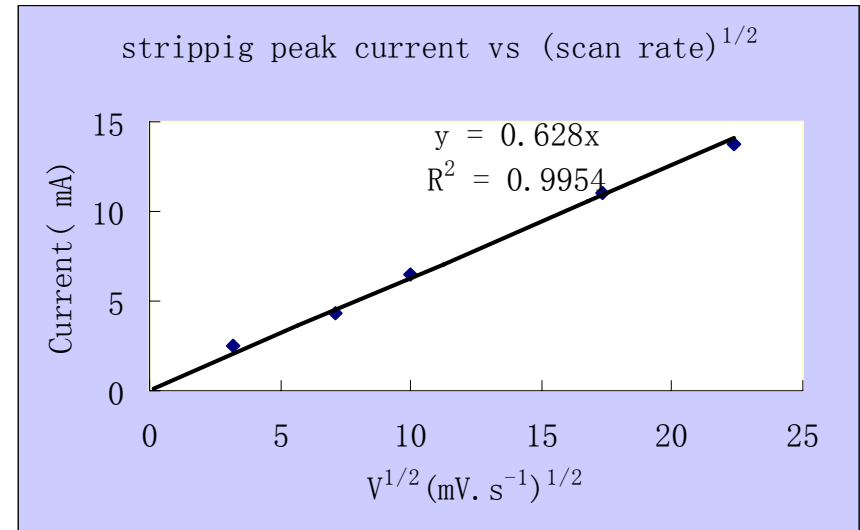
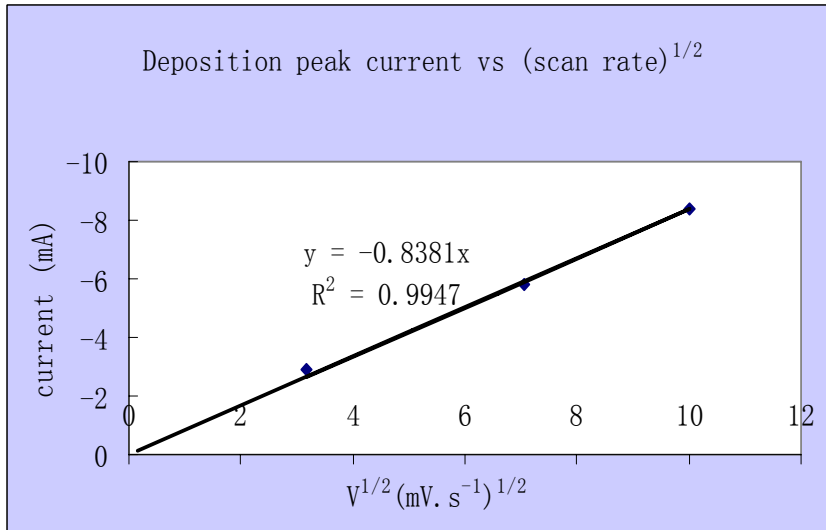
onset Ni reduction potential is 0.6V vs  
Fe<sup>2+</sup>/Fe

Electrolyte composition:

$\text{Na}_2\text{O} + \text{B}_2\text{O}_3 + \text{SiO}_2 + 5\% \text{ NiO}$

WE: Pt (0.12 cm<sup>2</sup>)

# Ni deposition is quasi-reversible

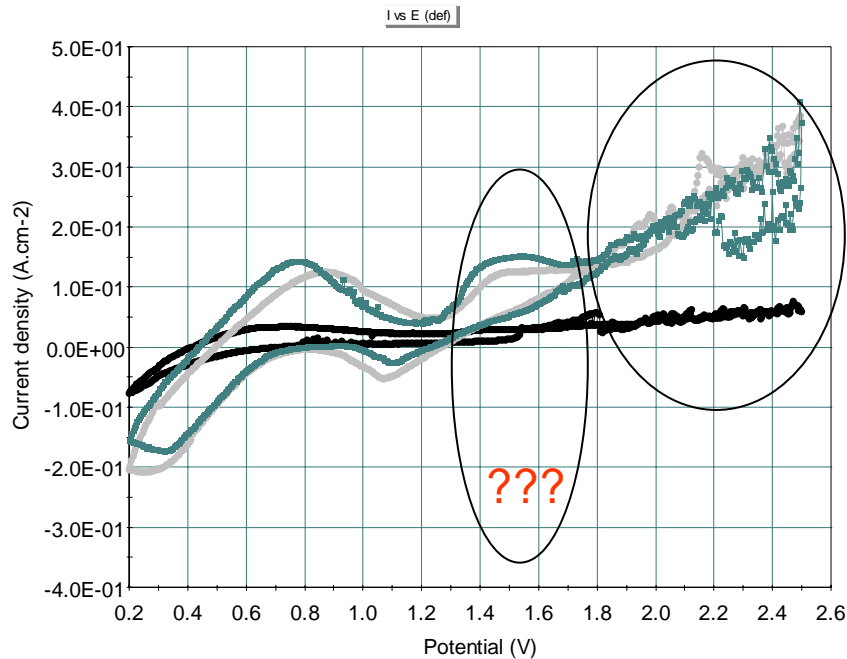


Deposition and stripping peak potentials change with scan rate. So electrode process is controlled by a mix of diffusion-controlled mass transport of  $\text{Ni}^{2+}$  and a slow step at the electrode/electrolyte interface



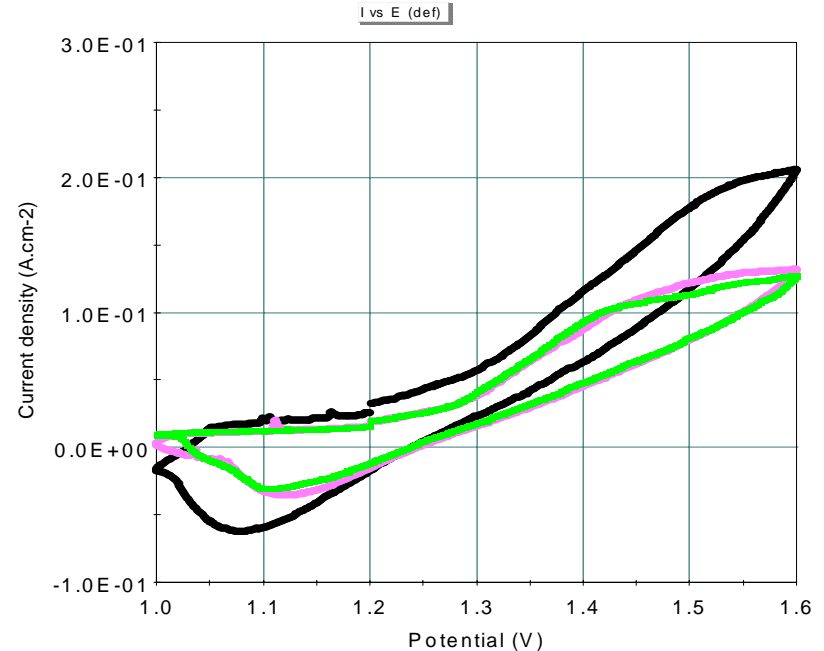
# Complex oxygen-ion adsorption and oxygen evolution

Electrolyte composition:  $\text{Na}_2\text{O}+\text{B}_2\text{O}_3+\text{SiO}_2+\text{NiO}$



Scan rate(mV/s) 10,50, 100

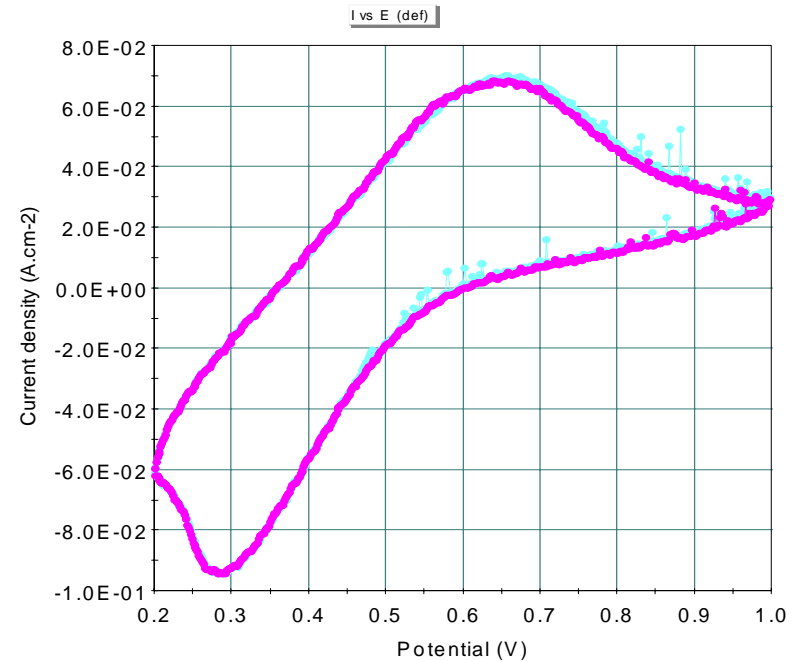
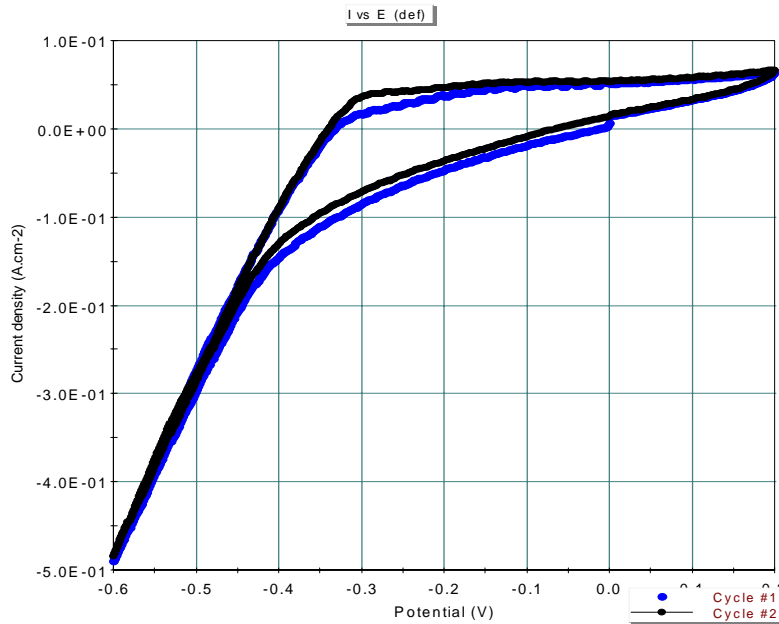
Oxygen evolution



Scan rate( mV/s ) :300, 100, 50  
we speculate the peaks related to

Complex oxygen ion adsorption and  
desorption

# The potential difference between Na and Ni deposition



Electrolyte composition

Na<sub>2</sub>O+B<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>

WE:Pt

Scan rate: 50mV/s

Electrolyte composition:

Na<sub>2</sub>O+B<sub>2</sub>O<sub>3</sub>+ SiO<sub>2</sub>,+NiO

WE:Pt

Scan rate :50mV/s

# Summary

- Potential window of Supporting electrolyte sustains Ni deposition from NiO.
- Ni deposition possible from oxides melts
- Ni deposition is controlled by a mix of
  - diffusion-controlled mass transport of Ni<sup>2+</sup>
  - and a slow step at the electrode/electrolyte interface,

# Acknowledgments



**Prof. Sadoway and members of Sadoway group, especially  
Prof. Dihua Wang, Mr. Andrew J. Gmitter, Mr. Guenter Arndt,  
Ms. Hilary Sheldon**

**Thank you for your attention**