Mo/Na_xTiO_2 Mixed Conducting Electrodes for the Alkali Metal Thermal to Electric Converter

M. A. Ryan, R. M. Williams, B. Fiebig, A. Kisor, L. Lara,
R. H. Cortez, M. L. Homer and V. B. Shields

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

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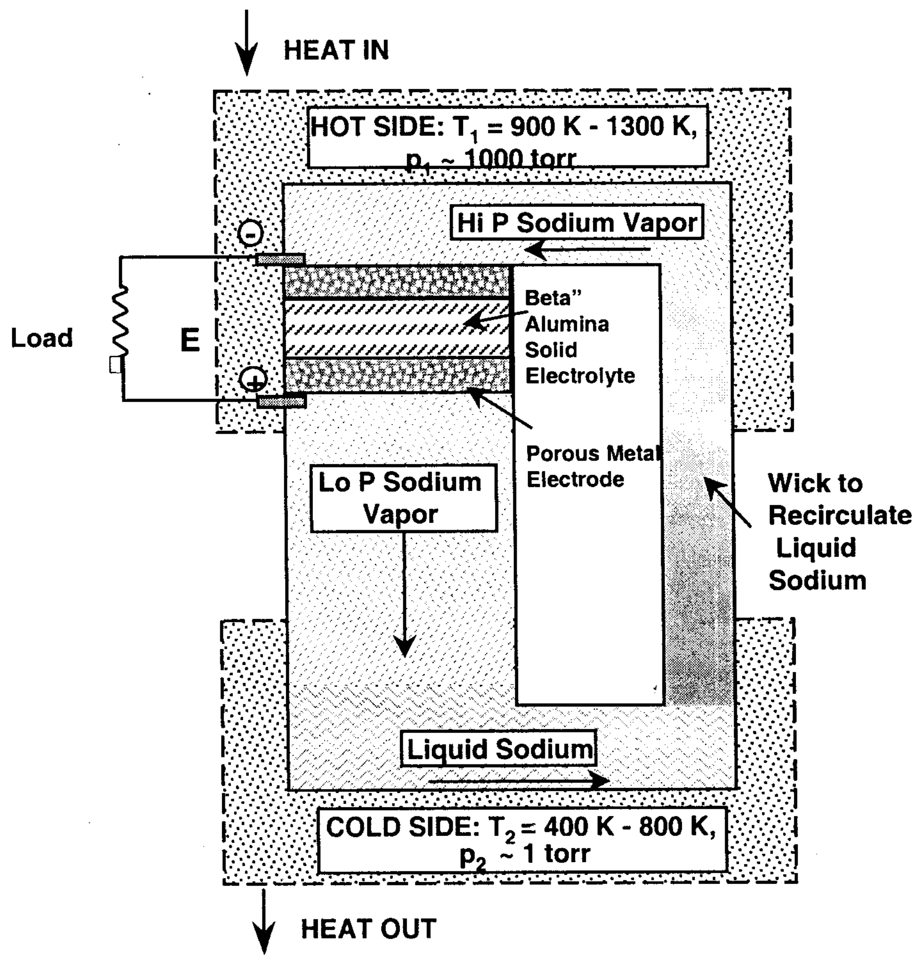
AMTEC - The Alkali Metal Thermal to Electric Converter



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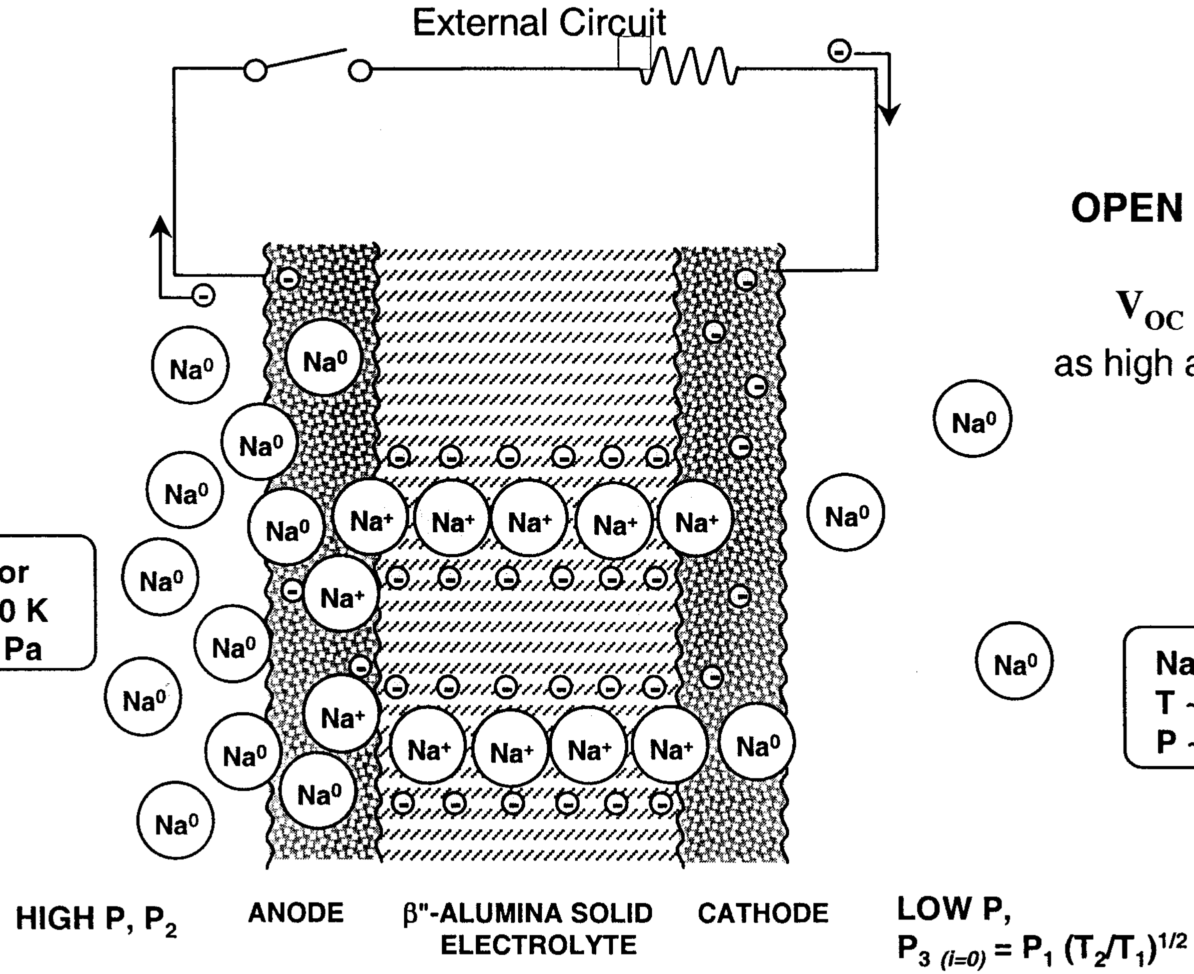


Na Vapor
T ~ 1150 K
P ~ 10^6 Pa

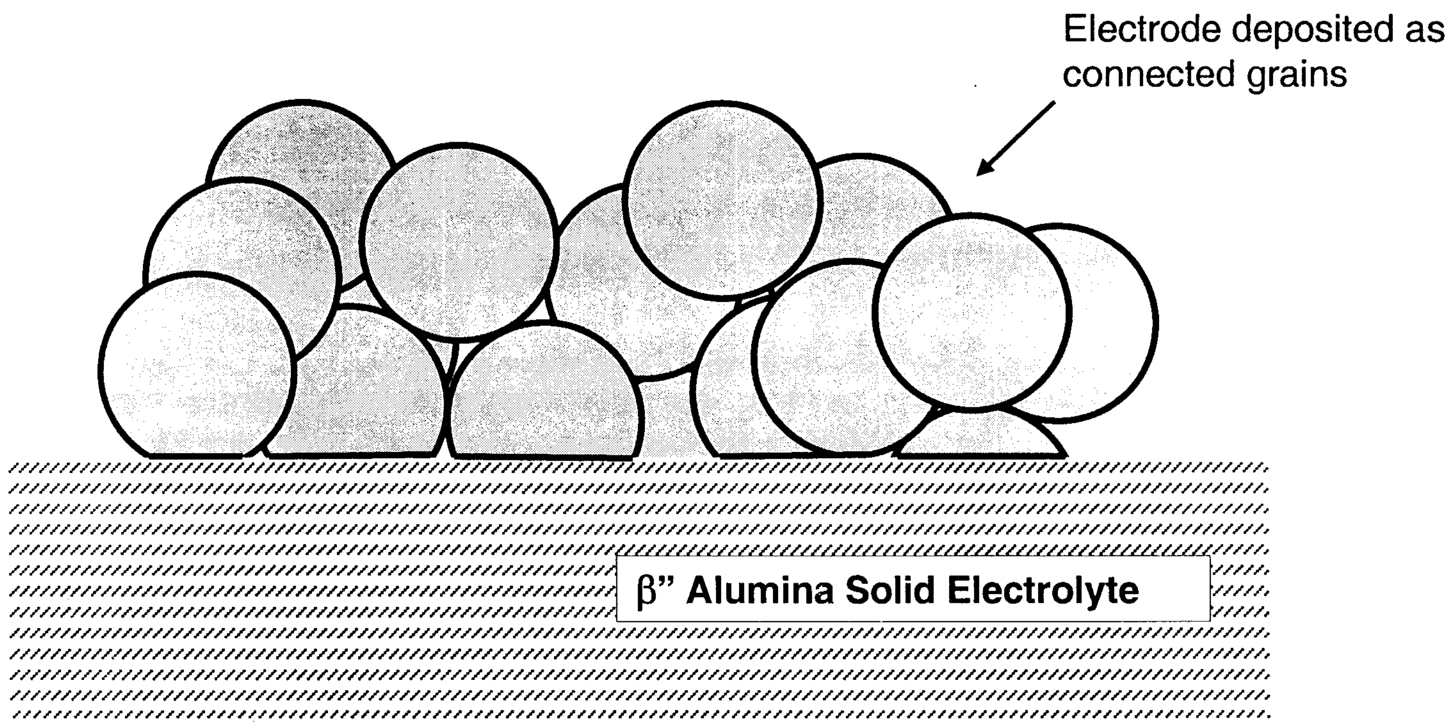
OPEN CIRCUIT VOLTAGE

$$V_{OC} = RT_2/F\ \ln(P_2/P_3)$$

as high as 1.6 V for a single cell

Na Vapor
T ~ 1150 K
P ~ 10 Pa

AMTEC Electrochemical Cell
Electrode Grains on Electrolyte Surface



AMTEC Electrode Performance

Electrode performance parameters:

B **Exchange Current Normalized to Sodium Pressure**

a measure of the facility with which sodium ions and electrons recombine in the three-phase interface at the electrode - electrolyte interface

$$B = \frac{J_0^0 T_{el}^{1/2}}{P_{el}} = \left[\frac{T_{el}}{P_{el} P_{Na}}\right]^{1/2} \left[\frac{R T_{el}}{R_{ACT} F}\right]$$

G **Morphology Factor**

a measure of the resistance to sodium atoms leaving the electrode and reaching the condenser; can be related to pore length (ℓ /m), pore diameter (**a** /m) and number density of pores (**N** /m^{-2}), and to current in the transport region of the iV curve

$$G = \left(\frac{P_{Na} (T_2/T_1)^{1/2} F}{j_{lim} (2\pi M R T_2)^{1/2}} - 1\right) \frac{8\pi}{3} = \frac{\ell}{a^3 N}$$

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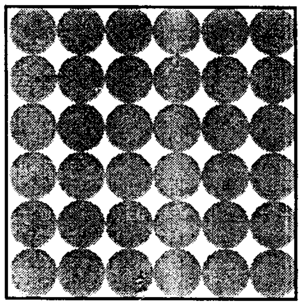
Cathode Grain Growth

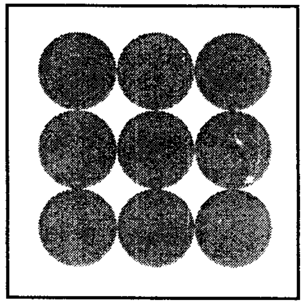
Exchange Current, B	**measure of electrode performance changes over time; at time t, $B_t \alpha \sqrt{r_t}$**
Sodium reduction	**at grain perimeter at electrode/ BASE interface**
Grain Growth	**activated by temperature and impurites**

SIMPLE MODEL OF GRAIN GROWTH: COALESCENCE OF SPHERES

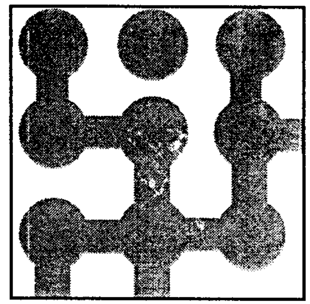


Contact Perimeter =
36 $(2\pi r_0)$
21% of area void

Grains join
2 times →



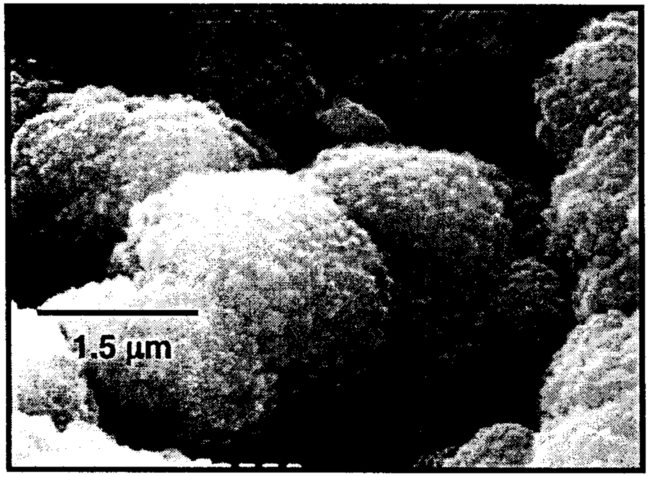
Contact Perimeter
9 x $(2\pi(1.59r_0))$ = 14 $(2\pi r_0)$
50% of area void



Contact Perimeter =
14 $(2\pi r_0)$ + bridges - "orphans"
50 - 60% of area void

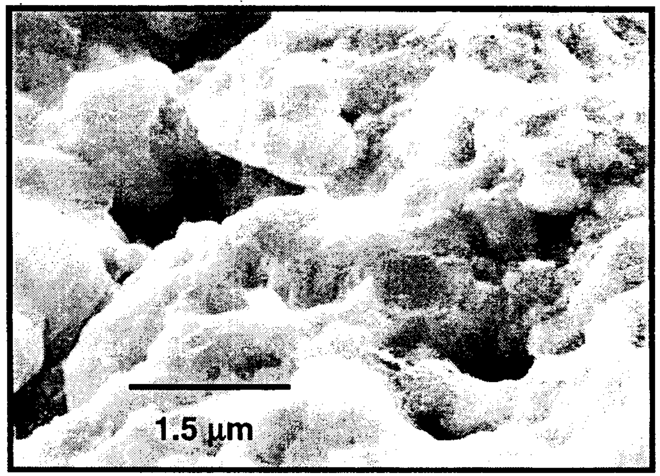
AMTEC Electrodes - TiN, RhW and Mo

TiN



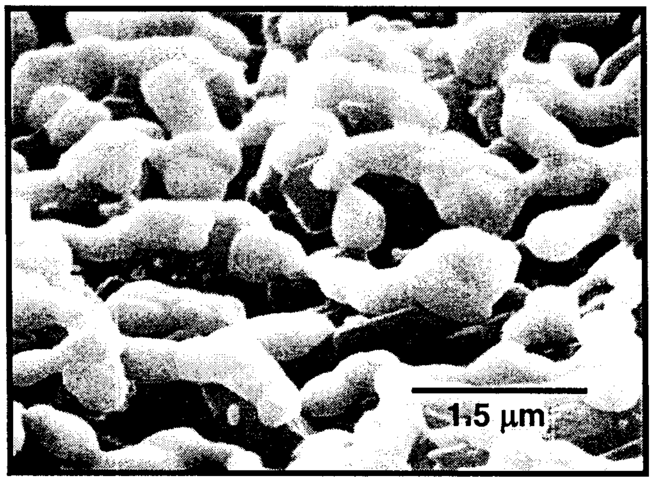
1800 hrs/ 1170 K / Na_V / Ti lined

$Rh_{2.5}W$



3000 hrs/ 1170 K / Na_V / Nb1%Zr lined

Mo



350 hrs/ 1100 K / Na_V

AMTEC Electrode Performance

Electrode Performance Enhancement

- ✦ Increase electronic conductivity in the electrode (R_{sh})
- ✦ Choose electrode material with largest exchange current, B (RhW)
- ✦ Increase sodium transport through electrode
  - Increase pore size ----> Decreased electronic conductivity
  - Provide ionic conduction to Na^+
    - ✲ ions move away from interface to combine with electrons, decreasing resistive losses and increasing B
    - ✲ ions move away from interface, decreasing transport losses and increasing G

AMTEC Electrode Performance

Electrode Performance Enhancement

- Sodium molybdate is an ionic conductor for Na^+. Adding it to Mo electrodes results in enhanced performance (increased B, decreased G)
- Similar effect with tungstate in W electrodes
- Both molybdate and tungstate evaporate in a few hours of operation at 750 - 800 °C (Melting points 687, 698)

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TiN AMTEC Electrodes

- TiN electrodes, especially thick, slurry applied electrodes, have better sodium transport than would be expected
- Ti-O compounds including TiO_2 have been found in TiN electrodes before and after operation (XRD and EDS/WDS)
- Several compositions of Na-Ti-O have been reported, including several Na_xTiO_2 compounds, with $.1 < x < .5$
- Na_xTiO_2 compounds are electronically conducting with conductivity dependent on Na content; some have been reported to be ionically conducting to sodium.
- As TiO_2 is present in TiN electrodes, it may be participating in the electrode performance by providing ionic conduction for Na^+ as well as additional electronic conduction.

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Conductivity of Na_xTiO_2

FORMATION OF Na_xTiO_2

Hours at 550°C	p_{Na}	Conductivity
0	3 Pa	.05 S/cm
1	3 Pa	.2 S/cm
24	6 Pa	.4 S/cm
48	2 Pa	.2 S/cm
72 (745°C)	.4 Pa	1 S/cm

Mo/Na_xTiO_2 Mixed Conducting Electrodes

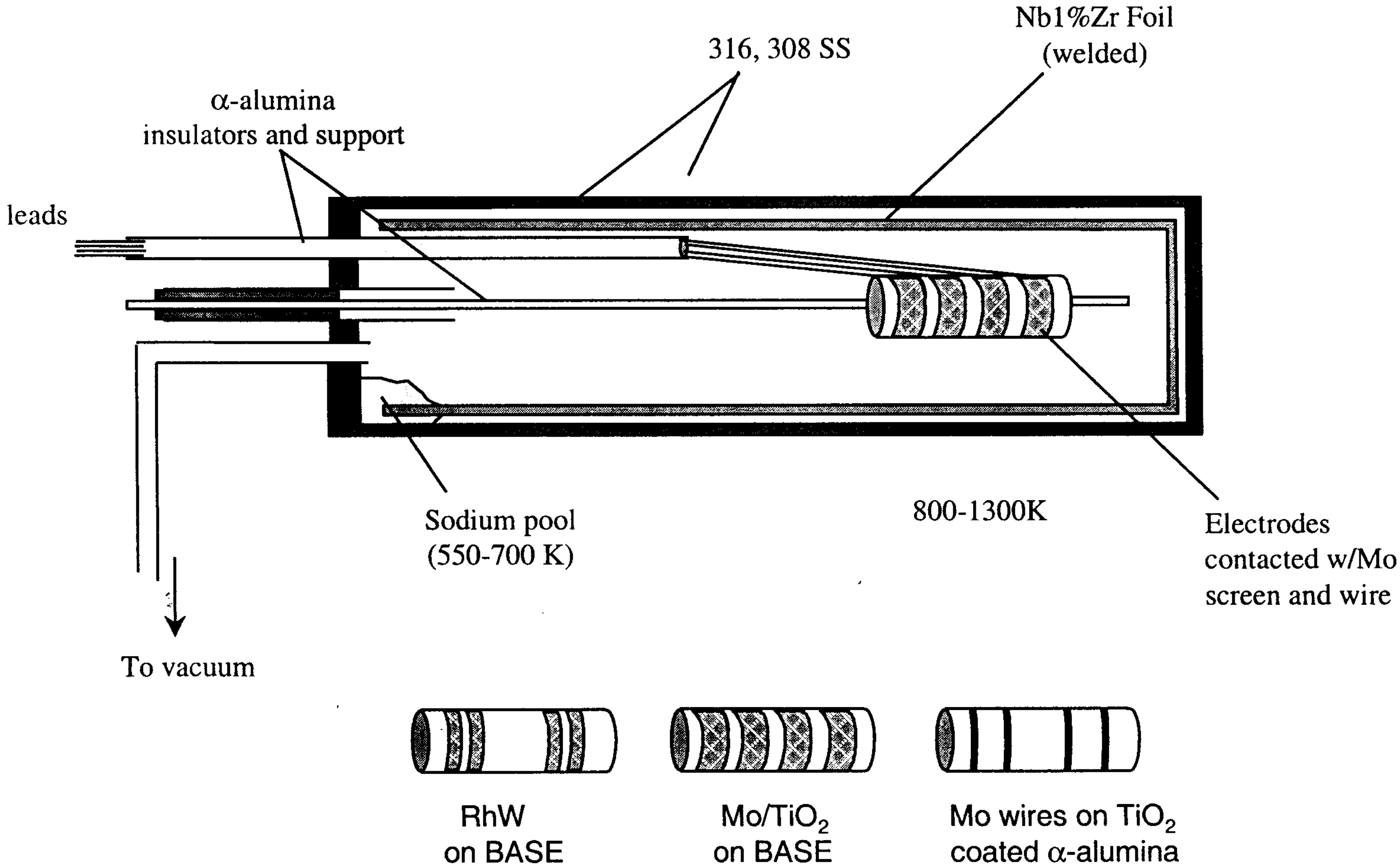
Experimental Conditions

TiO_2 powder (anatase) exposed to 100 Pa Na vapor at 900 °C for 100 hours reacts to form $Na_{0.5}TiO_2$, determined by gravimetric analysis and XRD

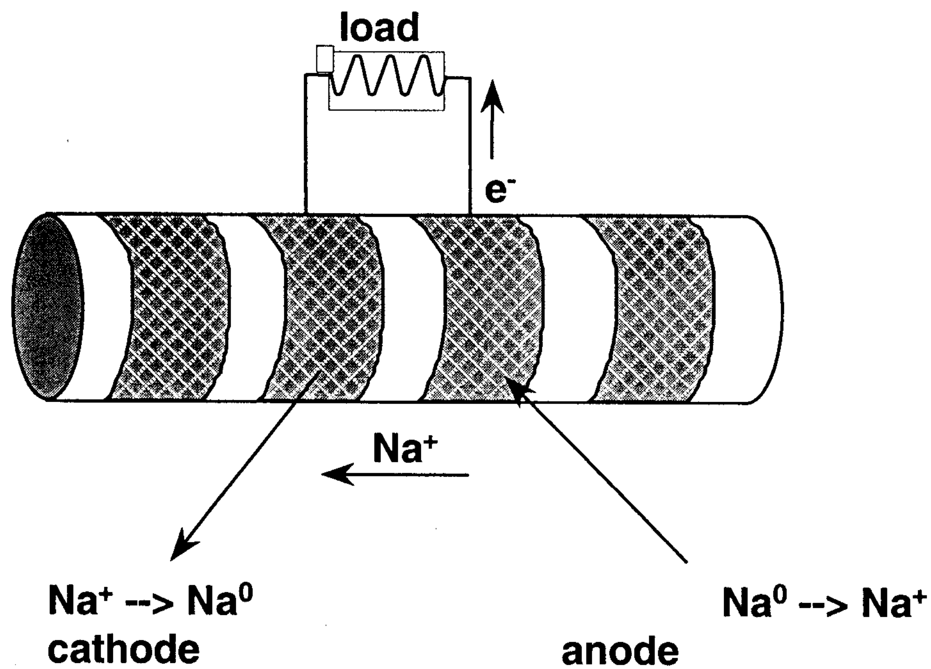
- **Three samples to operate ~ 1500 hours at 700 - 850 °C, 0.01 - 5 Pa Na pressure**
  - **5 mm thick layer of TiO_2 on α-alumina contacted with four 350 mm Mo wires to measure Na_xTiO_2 conductivity**
    Conductivity depends on Na content, thus Na pressure
  - **1 mm thick RhW films in four electrodes on beta"-alumina**
    RhW is a well characterized electrode used for comparative performance info. It is the electrode material with the best performance (B, G) tested so far
  - **5 mm thick layer of Mo mixed with TiO_2 in four electrodes on beta"-alumina**
    Mo electrode performance is well understood; differences in performance of Mo/TiO_2 may be attributed to the effect of TiO_2 or Na_xTiO_2
    50/50 (w/w) Mo and TiO_2 powders mixed with organic cement as a slurry and painted onto BASE. Fired in vacuum 2 hours at 1000 °C
- **All three samples mounted in a single chamber in a sodium vapor atmosphere, tested in two or four electrode configuration (iV curves and EIS); iV to calculate G and EIS for B**

Sodium Exposure Test Cell

Refractory Metal Sleeve Shielded Sodium Exposure Test Cell
Low Pressure Sodium Gas



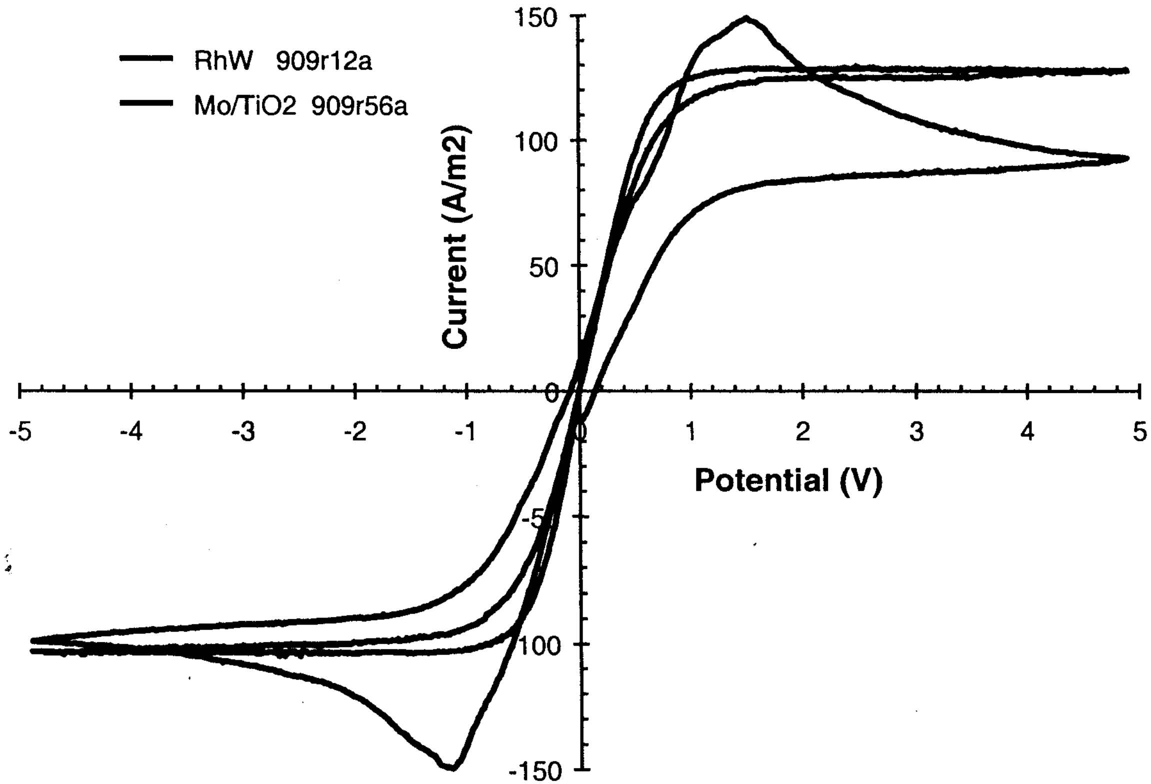
Sodium Exposure Test Cell
Electrochemical Cell



Voltage is controlled while current is measured in a typical 2-probe iV curve. Sodium ions travel axially along the BASE surface from the anode to cathode. Either electrode can function as anode or cathode, depending on the potential difference between them.

Mo/Na_xTiO_2 Mixed Conducting Electrodes

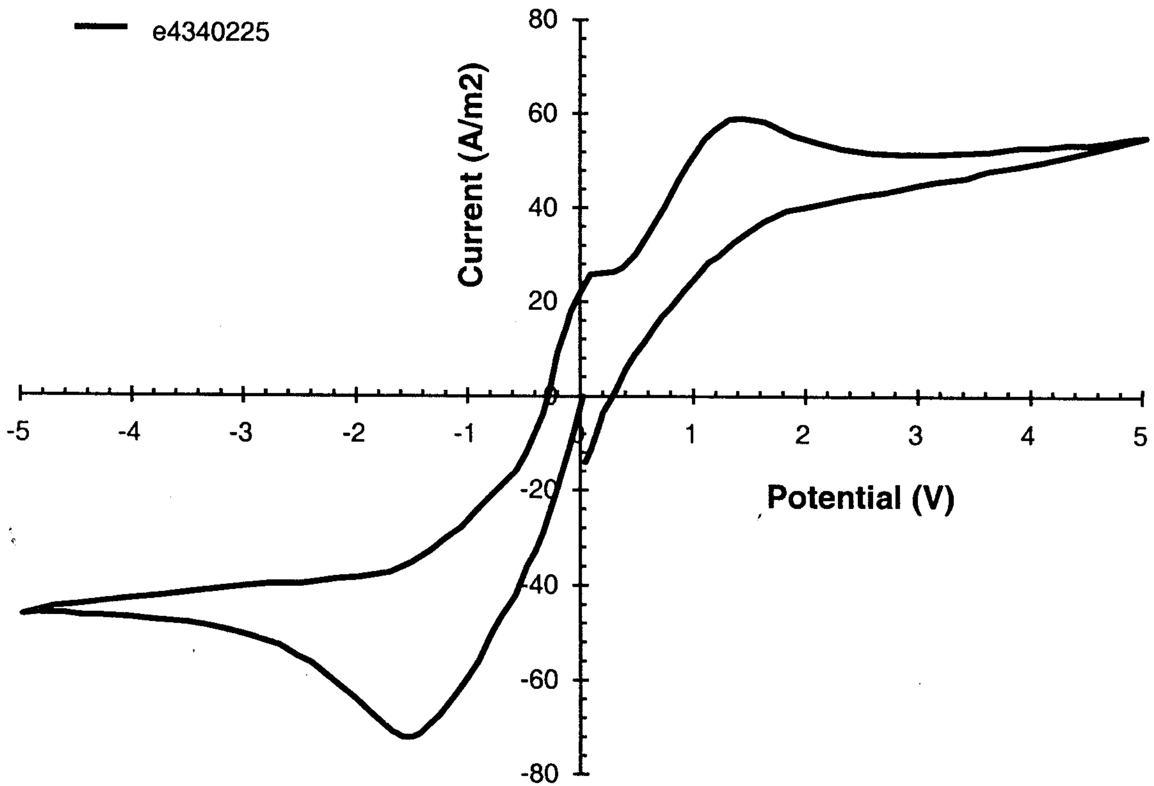
RhW and Mo/TiO_2 electrodes
Tel = 841 °C = 1114 K
TNa = 192 °C = 465 K
pNa = .022 Pa



TiN/Na_xTiO_2 Mixed Conducting Electrode

TiN electrode

T_{el} = 935 °C = 1208 K
T_{Na} = 150 °C = 423 K
p_{Na} = .002 Pa



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Mo/Na_xTiO_2 Mixed Conducting Electrodes

Conductivity of Na_xTiO_2 ~ 1 S/cm at 750 - 850 °C and 0.03 - 2 Pa pNa

Ionic and electronic components of conductivity cannot be separated

- Mo/TiO_2 electrodes in this experiment show redox waves ~ 1.2 V. This wave is not caused by oxidation of the Mo in the electrode. Wave is attributed to Na intercalation/deintercalation in TiO_2.
- TiN electrodes operated at low sodium pressure show similar waves at similar potentials.
- G for mixed Mo/TiO_2 electrode operated at 840 °C for > 900 hours calculated from iV cureves to be 5-10, indicating enhanced sodium transport; Mo thin films, G ~ 20-30
- Mo/TiO_2 electrodes have an exchange current, B, approximately equivalent to that of RhW, the best performing electrode tested.

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Conclusions

- Performance of a thick film mixed conducting electrode Mo/Na_xTiO_2, is substantially better than that of a thin film Mo electrode
- The Mo/Na_xTiO_2 electrode is robust and does not degrade in performance over 1500 hours of operation. Mo alone degrades owing to grain coalescence and decreased electrode area and conductivity.
- Conductivity of Na_xTiO_2 is a function of sodium pressure in the cell; changes in conductivity induced by change in pNa are reversible
- Na_xTiO_2 conductivity at a given temperature and pNa does not change over 1500 hours of operation above 800°C

➔ Na_xTiO_2 can facilitate sodium transfer through the AMTEC electrode as an ionic conductor, resulting in enhanced electrode performance.

➔ Metal mixed with TiO_2 and applied as a paint or slurry can be used as an inexpensive, robust AMTEC electrode