Electrochemical Power Sources for Extreme Temperature Operation

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Electrochem
LITHIUM BATTERIES

Introduction

Requirements for Electrochemical Power Sources

1. Compatibility of components: anode, cathode with electrolyte over needed temperature range and time

2. Ionic movement: mechanism for transport of cations from anode through electrolyte and into cathode, or anions from cathode through electrolyte into anode

3. Anode contributes positively charged species to electrolyte; cathode contributes negative species; electrolyte is able to absorb products; mechanism for transport of ionic species exists throughout electrolyte

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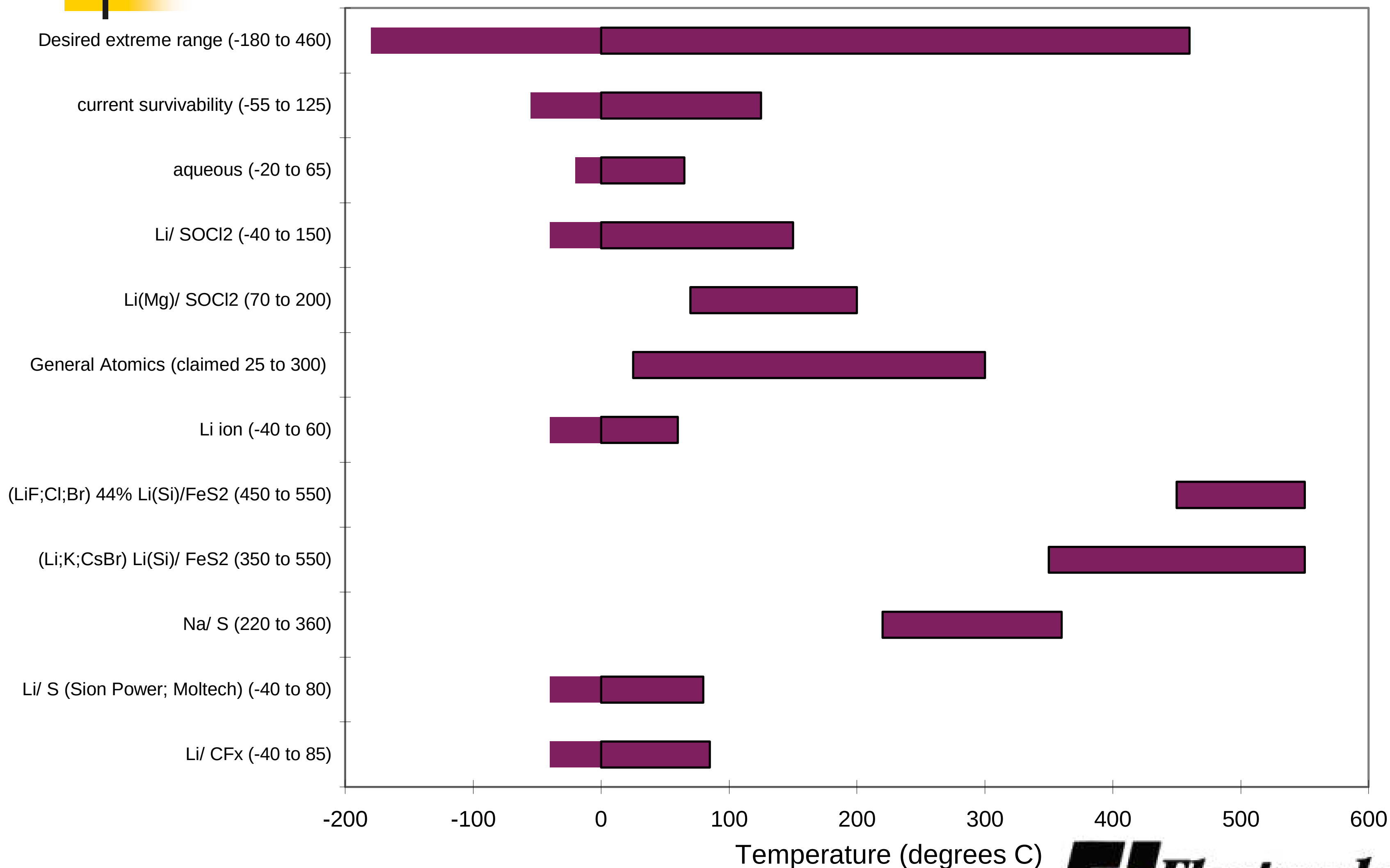
Overview: battery systems



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Properties

Li/ $SOCl_2$

(-40 to 150 deg. C.)

Advantages

- Moderate rate (up to 3 mA/ cm^2 over most of range)
- No solid cathode (Stability improved; wider temp. range, solvent is also cathode, can be heated beyond boiling point under pressure without decomposition)
- Mature technology (early limitations mitigated)
- Safe, when correctly designed (Li/ SO_2 is deadlined)

Limitations

- Melting point of Li = 180^0C. Dangerous beyond this!
- Slow startup on reuse (address Li passivation)

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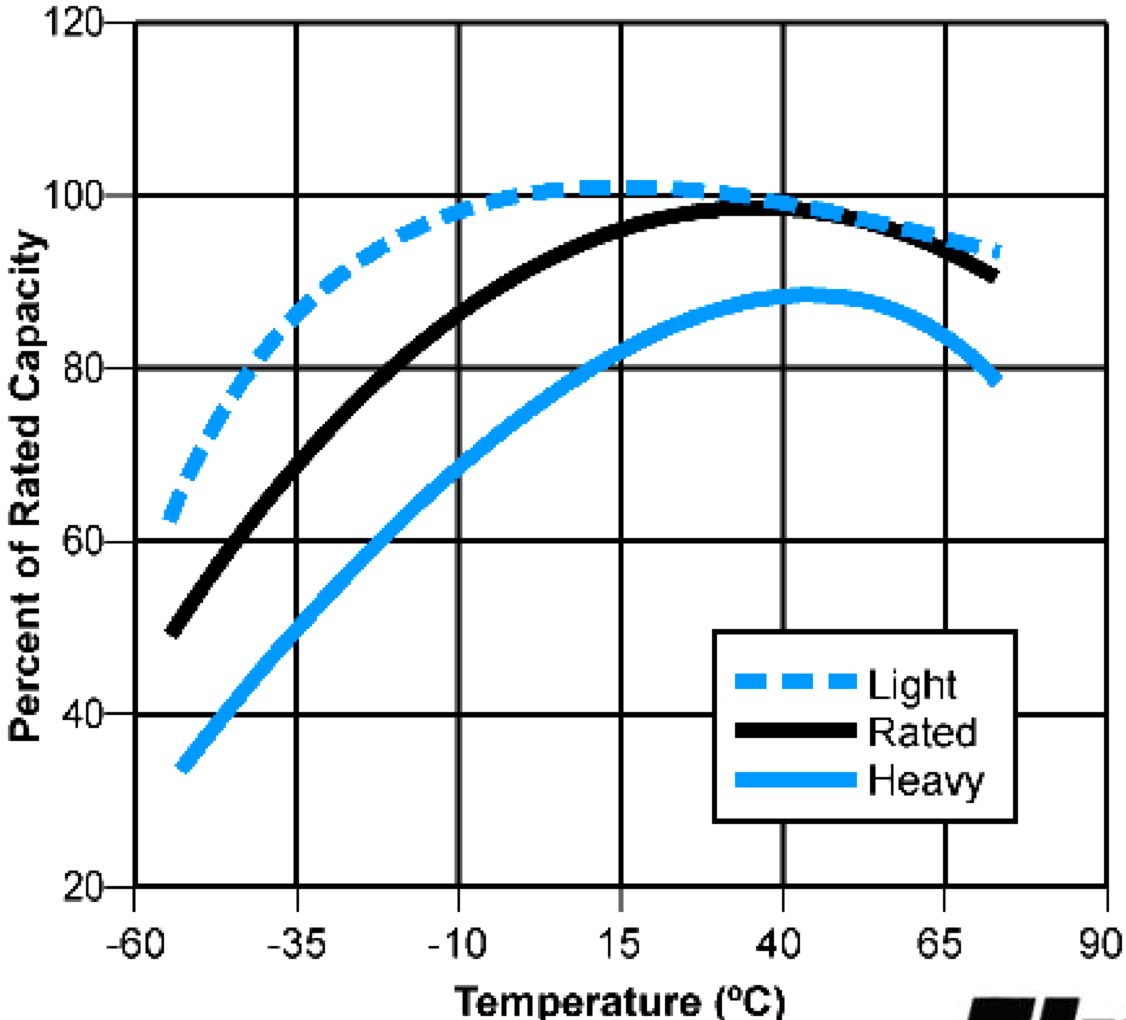
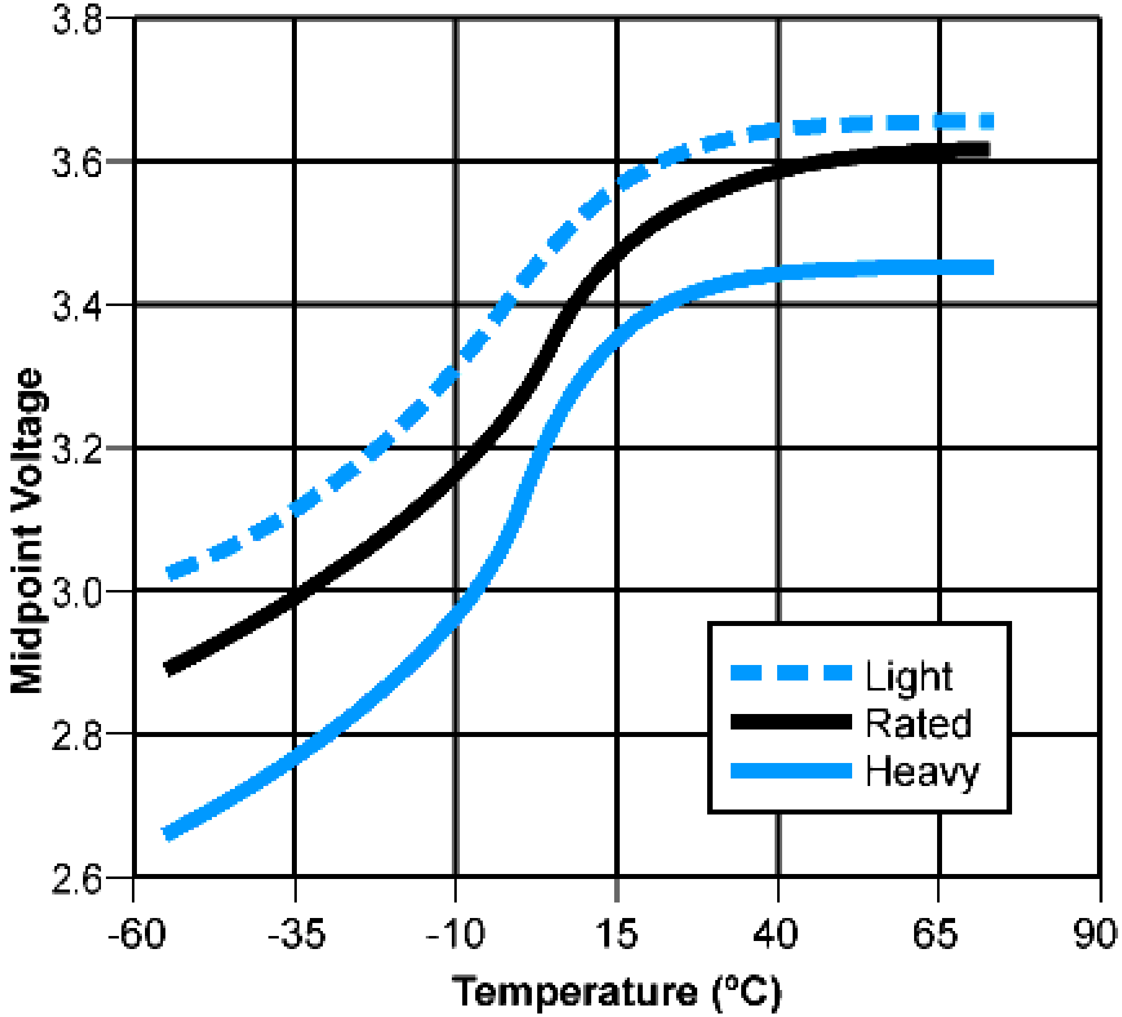
Electrochem BCX85 cells (wound electrodes; $SOCl_2$, bromine)



Electrochem BCX85 cells (wound electrodes; $SOCl_2$, bromine)



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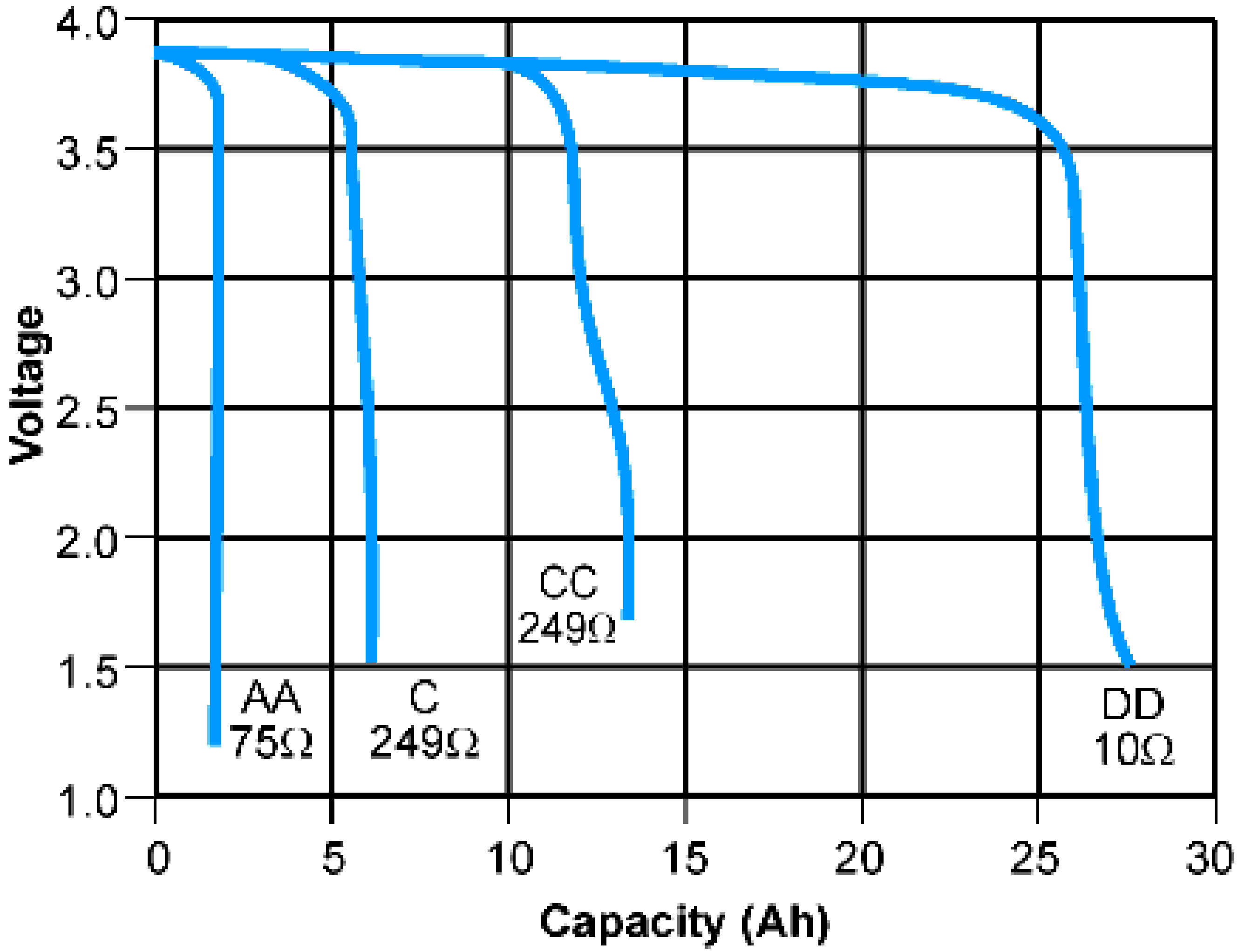
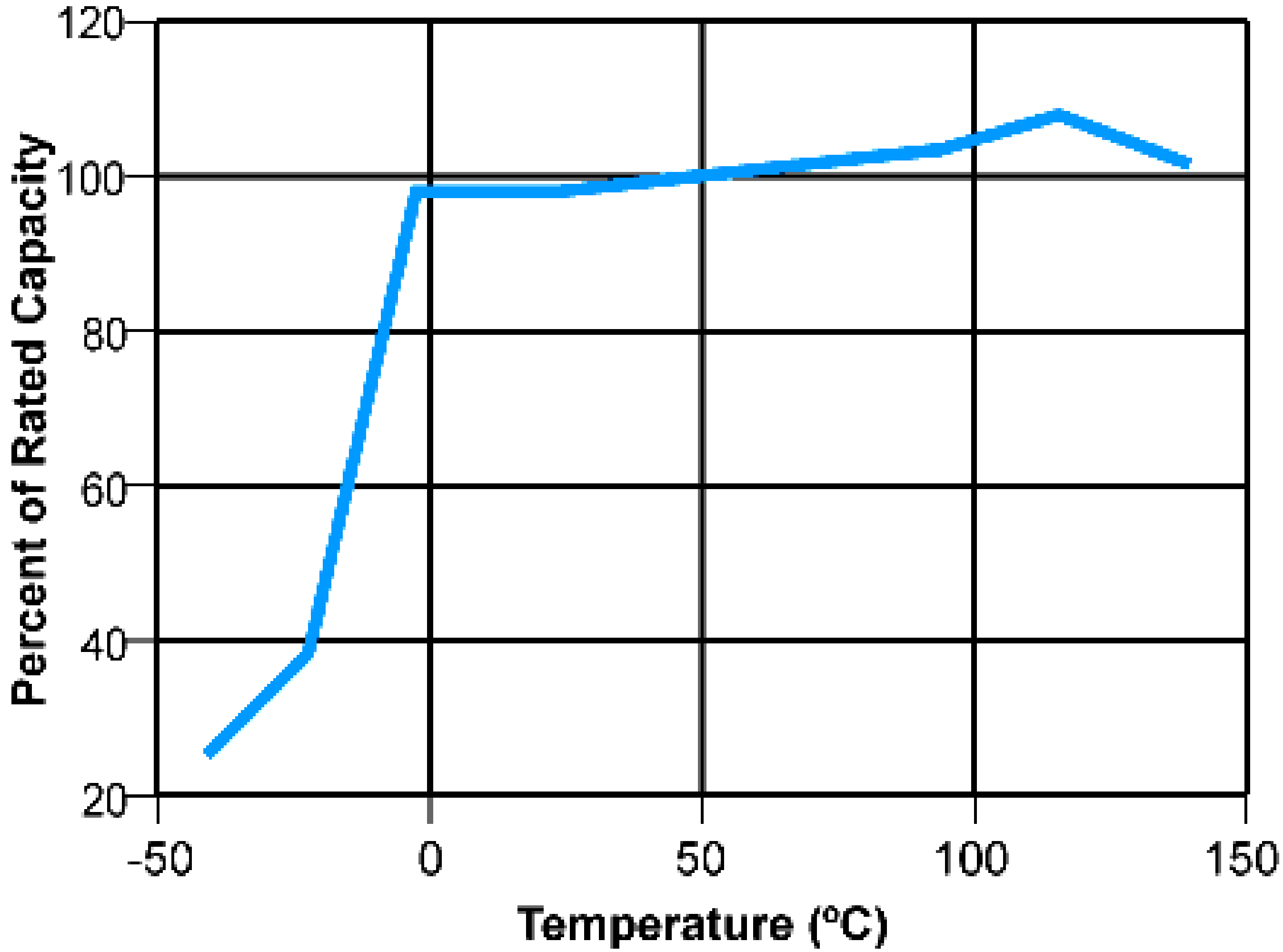
Electrochem PMX 160/165 (wound, 150ºC., SO_2Cl_2)



Electrochem PMX 160/165 (wound electrodes, SO_2Cl_2)



Properties

Li(Mg)/ $SOCl_2$
(70 to 200+ deg. C.)

Advantages
- Extended high temp. range (*you* choose how much)

Limitation
- Lower I and V at lower temp. (limited by diffusion of Li/ corrosion of Mg)

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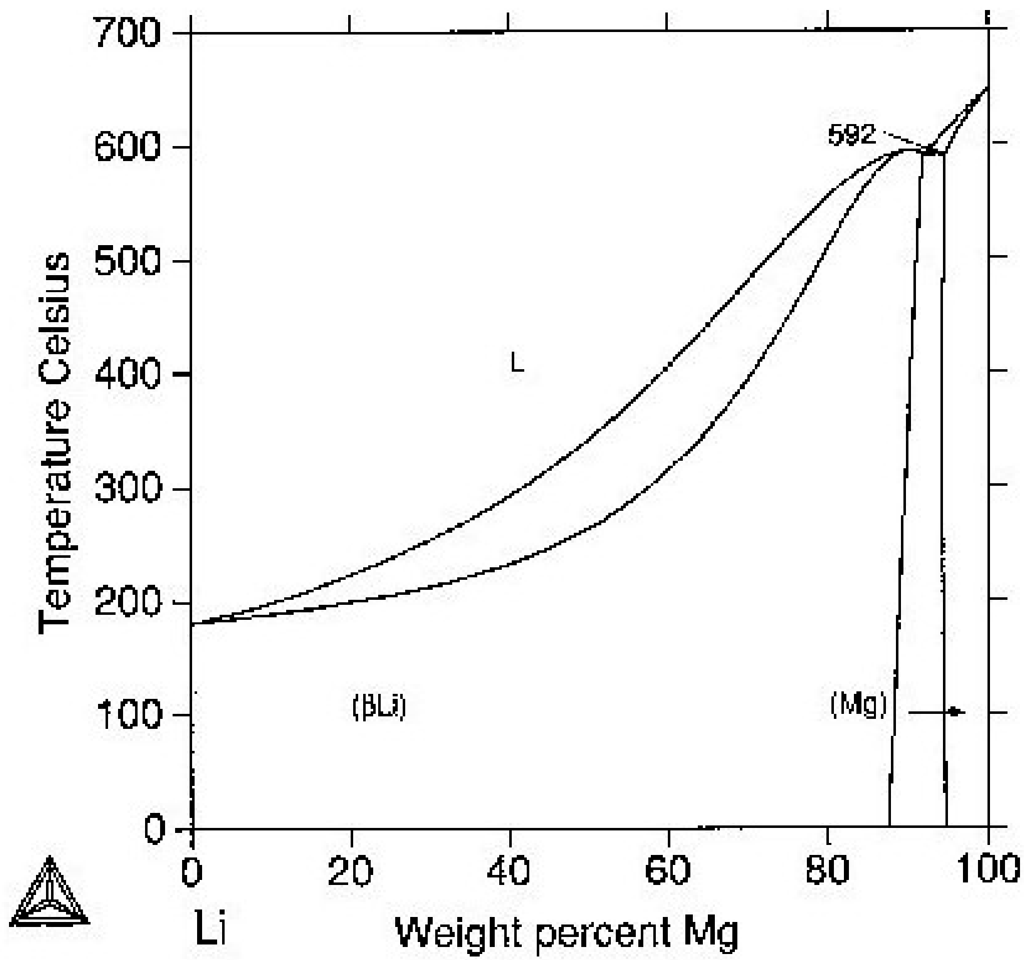
Properties: Lithium/ magnesium alloy system



Georgia Tech ASM/TMS; N. Saunders, Calphad **14**, (1990) 61-70

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44% Li(Si)/FeS_2

(450 to 550 deg. C.)

Advantages

- High rate (well over 1 A/ cm^2 at 500^oC.)
- Li/Si eutectic melts at 592^oC; no other phases to 100% Si
- Mature technology (Reliable. Replaces Ca/ $CaCrO_4$. Used in vehicles.)

Limitations

- Anode polarizes below 450^0C. Salt melts at 426^oC.
- Cathode polarizes above 550^0C.
- Only alkali salts are stable (no $AlCl_4^-$ or Ca allowed)
- Thermal management (heat idle cells; cool during use)

Ronald A. Guidotti, Proceedings of the 35th IECEC (2000) pp1276-86

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Properties

Heavy Alkali Li(Si)/FeS2

(350 to 550 deg. C.)

Advantage

- Wider operating temperature range (than Li only system)

Limitation

- Considerably lower rate capability (than Li only system)

Ronald A. Guidotti, Proceedings of the 35th IECEC (2000) pp1276-86

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Na/ S

(220 to 360 deg. C.)

Advantages

- Inexpensive materials (can be used in large facilities)
- High efficiency
- Rechargeable
- Mature technology (since 1984 in power plants, vehicles)

Limitations

- Sensitive to overcharge/ discharge
- Corrosion of materials
- Thermal management (heat idle cells; cool during use)
- Fragile; stationary use best (liq. Na/ solid Al_2O_3/ liq. S)

Properties

Li/ S

(-40 to 80 (?) deg. C.)
Sion Power Corporation, Tucson, AZ

Advantages
- Inexpensive materials
- Rechargeable
- High rate at low temperature
- Resistant to overcharge and overdischarge

Limitations
- Safety (?) Organic solvents including dioxolane and 1,2-dimethoxyethane are used
- Corrosion of materials (?) Sulfite esters limit Li corrosion (Mikhaylik, US 6,436,583 B1, Aug. 20, 2002)

Y.V. Mikhaylik and J.R. Akridge, J. Electrochem Soc 150 A306-A311 (2003)

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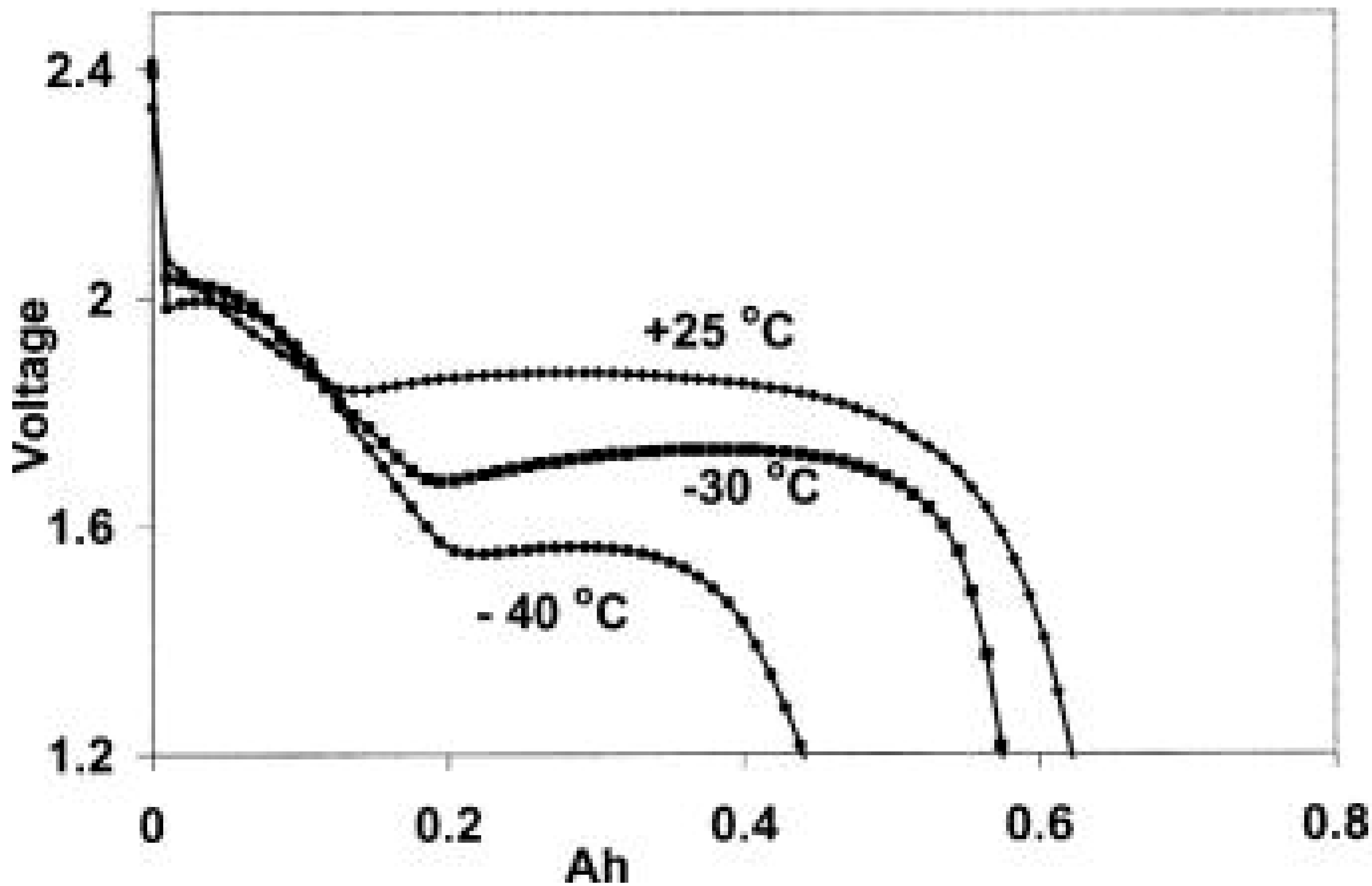
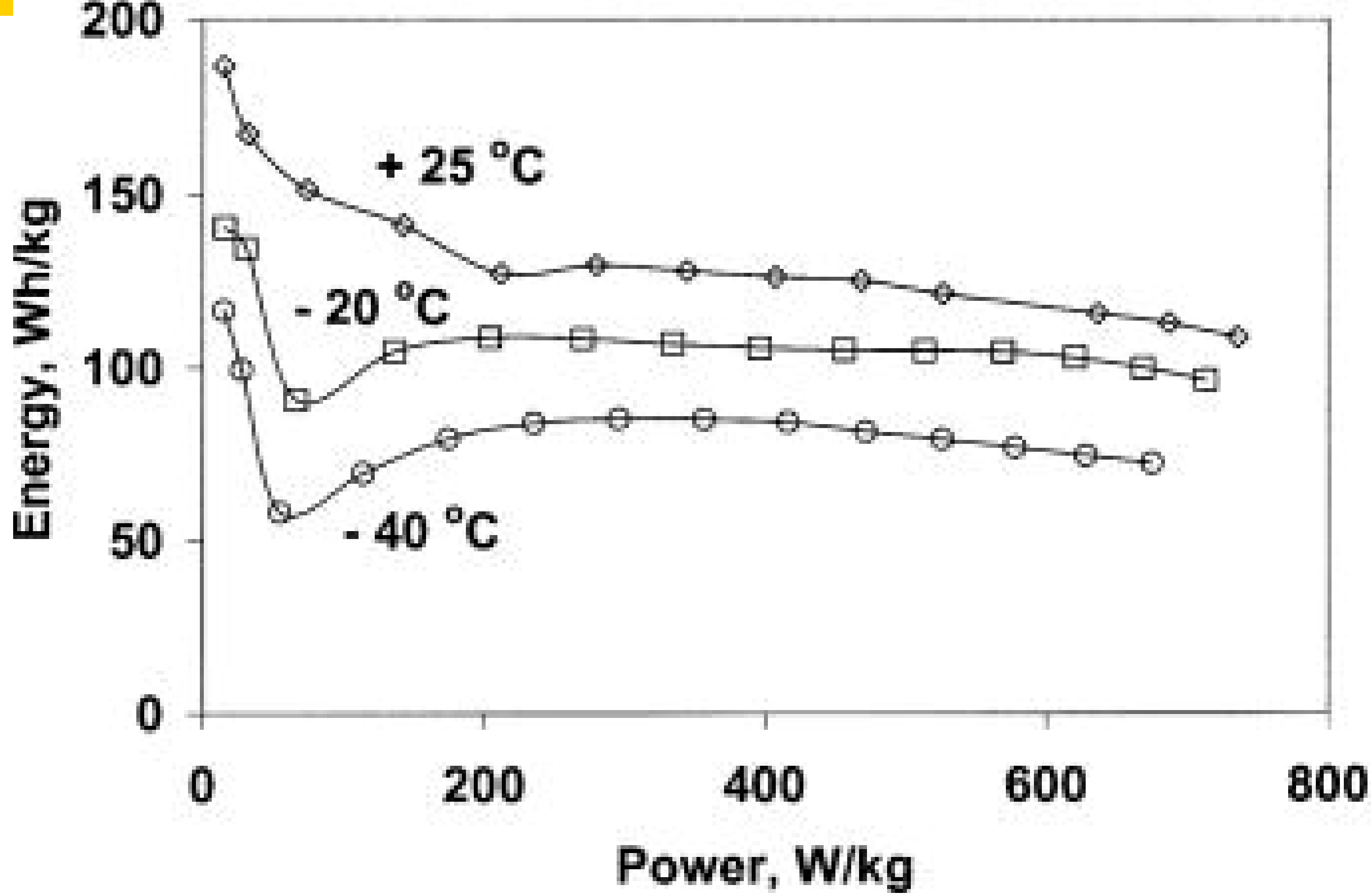
Sion Power low temperature Li/ S

50 x 36 x 7 mm prismatic. Discharge rate, 3.5 A (5C)



Sion Power low temperature Li/ S



Issues

Reactivity

Li: Unique. Reacts with electrolytes superficially. Coating, if insoluble, protects metal; allows only Li^+ through. But melts at 180°C.; more reactive towards organics above about 60°C. (can use $SOCl_2$; SO_2Cl_2)
Alloys: diffusion a problem below about 70°C. Molten alkali salts won't react; no film needed

Ca: Melts at 842°C., but salt film conducts anions. Get only 1 equiv/ mole, electrolyte loss. No filmless systems known except molten salts. (Mg also)

Al: Melts at 660°C., but films are insulators. Low melting salts exist, but organics are too reactive. Alkali $AlCl_4^-$ salts melt near 100°C., but acid electrolytes (excess $AlCl_3$) interfere with anode.

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Issues

Longevity

- Thermal cells cool off (originally for missiles; max life 5 minutes)
- Thermal cells: Higher temperature introduces corrosion of cell parts
- Oxyhalide cells: Improper design introduces “voltage delay” on startup after partial use; storage
- Self discharge

Energy density

- Thermal cells: use of squibs, heaters takes up space (better if ambient temperature is suitable)

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Issues

Mechanical stability

- Sodium sulfur cell is inside out: liquid, solid, liquid. The solid electrolyte is beta alumina….. The thinner the better for lower resistance. But the ceramic is fragile
- Sodium/ sulfur: Right side up is best

Resources

High/ low temperature battery websites:

batdesign.com
swe.com

Of particular note:

greatbatch.com
sionpower.com
sandia.gov