Assessment of Lithium-based Battery Electrolytes Developed under the NASA PERS Program

William R. Bennett
QSS Group, Inc.
and
Richard S. Baldwin
NASA Glenn Research Center

Recently, NASA formally completed the Polymer Energy Rechargeable System (PERS) Program, which was established in 2000 in collaboration with the Air Force Research Laboratory (AFRL) to support the development of polymer-based, lithium-based cell chemistries and battery technologies to address the next generation of aerospace applications and mission needs. The goal of this program was to ultimately develop an advanced, space-qualified battery technology, which embodied a solid polymer electrolyte (SPE) and complementary components, with improved performance characteristics that would address future aerospace battery requirements.

Programmatically, the PERS initiative exploited both interagency collaborations to address common technology and engineering issues and the active participation of academia and private industry. The initial program phases focused on R&D activities to address the critical technical issues and challenges at the cell level. A variety of cell and polymeric electrolyte concepts were pursued as part of the development efforts undertaken at numerous governmental, industrial and academic laboratories. Numerous candidate electrolyte materials were developed, synthesized and optimized for evaluation. Utilizing the component screening facility and the "standardized" test procedures developed at the NASA Glenn Research Center, electrochemical screening and performance evaluations of promising candidate materials were completed.

This overview summarizes test results for a variety of candidate electrolyte materials that were developed under the PERS Program. Electrolyte properties are contrasted and compared to the original project goals, and the strengths and weaknesses of the electrolyte chemistries are discussed. Limited cycling data for full-cells using lithium metal and vanadium oxide electrodes are also presented. Based on measured electrolyte properties, the projected performance characteristics and temperature limitations of batteries utilizing the advanced electrolytes and components have been estimated. Limitations for the achievement of practical performance levels are also discussed, as well as needs for future research and development.

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QSS Group, Inc., Cleveland, Ohio, 44135

Richard S. Baldwin

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Program Background

- DoD/NASA collaborative effort was formed in 1997 to enhance Li-ion liquid battery and cell performance.
- Lithium-based chemistries with solid-state and/or polymer-based components were envisioned to be enabling next-generation technologies.
- In FY 2000 NASA and the Air Force Research Laboratory expanded collaborative efforts to support development of polymer-based technologies.
- Advancement of next-generation technologies formed the basis of the Polymer Energy Rechargeable System (PERS) Program.
  – Participants selected in FY 2001 via a NASA Research Announcement (NRA)

Objective

Establish a world-class technology capability and U.S. leadership in polymer-based battery technology for aerospace applications.

<u>Anticipated benefits of PERS</u>

- simplified, lightweight designs
- intrinsic safety
- increased specific energy, energy density, life
- favorable manufacturing costs

PERS Program Participants

PERS PROGRAM SELECTED CONTRACTOR AND GRANTEES	
Covalent Associates	Advanced Lithium Polymer Electrolyte for Li-Ion Batteries
Eagle-Picher Technologies, LLC, Joplin, MO	Novel Host Material for Ceramic Electrolytes
EIC	Lithium Based Polymer Electrolyte Battery
Indiana University	Nanostructured Single-Ion SPE for Lithium Batteries
InvenTek	Development of Solvent-Free High Performance Li-Polymer
Lawrence Berkeley National Laboratory (LBNL)	Advanced Polyelectrolyte Separators for Rechargeable Lithium Batteries
LITHCHEM International	New Stable, More Conductive Solid Polymer Electrolyte
Lithium Power Technologies	Polymer Electrolytes for Solid-State Lithium Batteries
Lockheed Martin / Comsat	Lithium Based Polymer Battery Development
Max Power / Temple University	An Integrated Approach to Develop a High Energy Density Long Cycle Life Lithium Based Polymer Battery
Naval Air Warfare Center Weapons Division (NAWCWD)	New Solid Polymer Membranes for Rechargeable Lithium Batteries
National Center for Microgravity Research	Thermal Modeling of Lithium Based SPE Battery in Microgravity Applications
Northwestern University	Development of Highly Conductive Polyelectrolytes for Lithium Batteries
Physical Sciences, Inc.	High Performance Li-Ion Polymer Electrolyte with Pendant Anion Receptors
Texas Engineering Experimental Station (TAMU)	Advanced Li-Ion Polymer Batteries for Aerospace Applications
University of Minnesota	New Polymer Electrolyte Cell Systems
University of Utah	A Joint Simulation and Experimental Study of Nanocomposite Polymer Electrolytes
Yardney Technical Products	Development of a Lithium-Based Polymer Energy Rechargeable System for Future Space Applications
PERS PROGRAM GOVERNMENTAL PARTICIPANTS	
NASA Glenn Research Center (GRC)/University of Akron	Novel Molecular Architectures for Improved Solid Polymer Electrolytes for Lithium Polymer Batteries
Air Force Research Laboratory (AFRL) – WPAFB	Ionically-Conducting Channel Polymer Electrolytes
Jet Propulsion Laboratory (JPL)	Solid Polymer Electrolyte Development

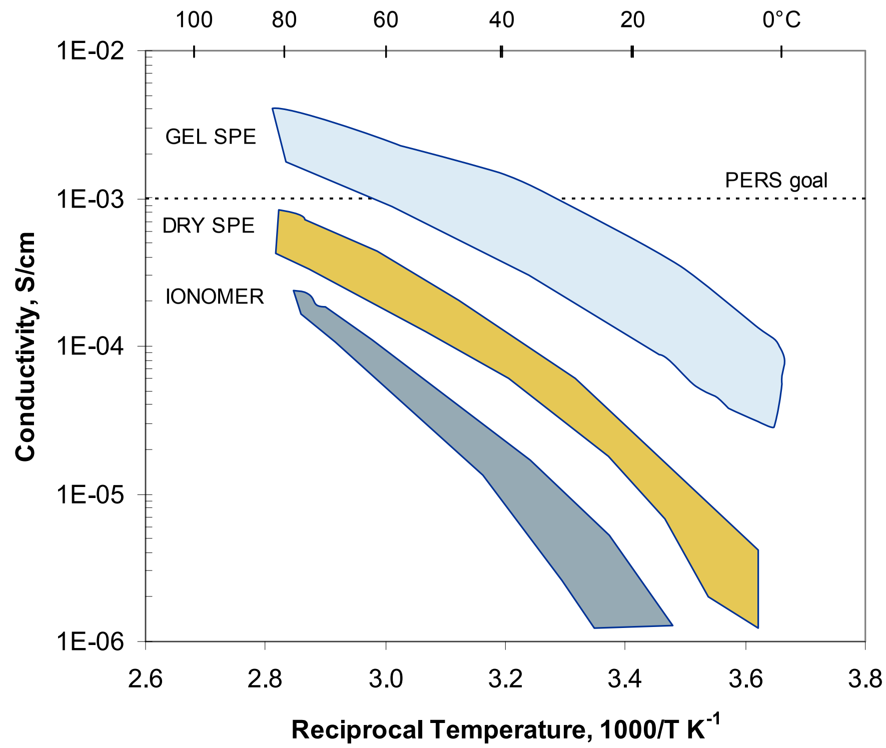
Goals for Electrolyte Development

GRC Testing Facility was expanded to screen and compare candidate PERS electrolytes in terms of critical properties:

- High ionic conductivity (~10^{-3} S/cm)
- Li^+ transference number approaching 1
- High salt diffusion coefficient
- Electrochemical Stability Window 0 to >4 V
- High Electronic Resistivity (>10^{12} ohm·cm)
- Favorable Interfacial Properties
- Stable transport properties
- Thermal and dimensional stability
- Mechanical toughness

Ionic Conductivity

- Gels approach PERS goal at room temperature.
- Dry SPEs approach goal at >80°C.
- Ionomers have lower conductivity due to immobilized anion.



Over 330 polymer electrolyte samples submitted (most based on PEO)

The best dry SPE (optimized for conductivity) = $5 \cdot 10^{-5}$ S/cm at 25°C

Ionomers not provided in sufficient quantity for supplemental testing

Transport Properties for Dry SPE

- Li^+ transference number (t_+^0) salt diffusion coefficient (D_s)
- Influence salt concentration gradients under polarization.
- Limiting current density, power production, electrode utilization and even life are affected.

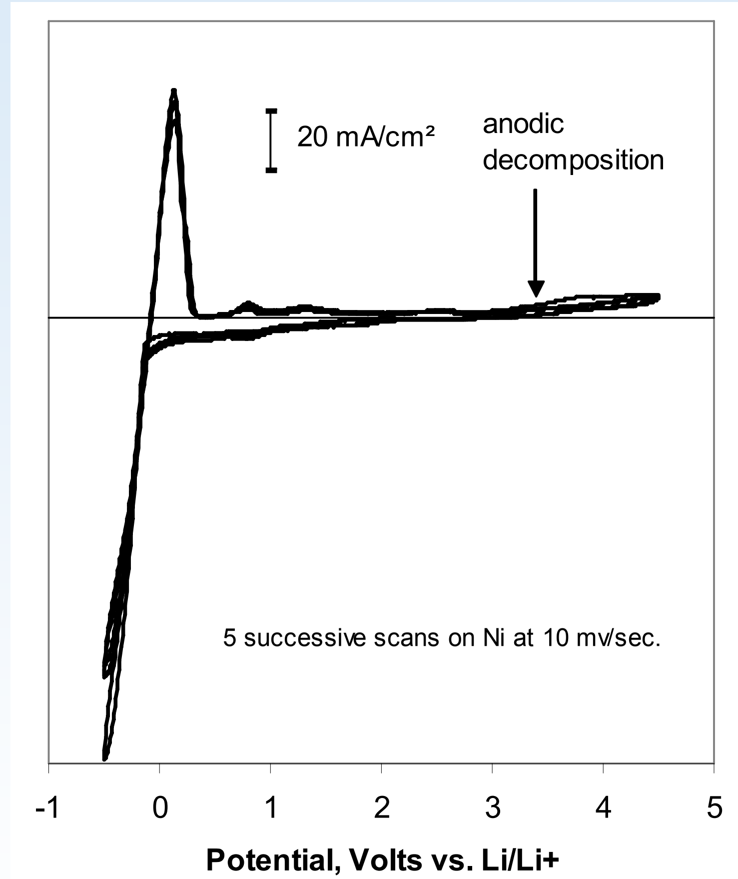
Representative values at operating temperature

	dry SPE at 80°C	Liquid electrolyte at 23°C
t_+^0	0.2	0.2-0.4
D_s, cm^2/s	10^{-8}	10^{-6}

salt diffusion coefficient is low in SPE, even at 80°C

Electrochemical Stability Window

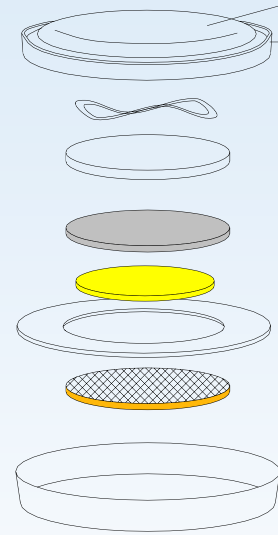
- measurements at 80°C shown for dry SPE optimized for conductivity.
- reasonable plating/stripping efficiency for Li metal .
- small oxidation current observed at +3.3 V
- salt and polymer makeup could be factors



anticipated compatibility with 3-Volt class electrodes

Full Cell Testing with Vanadium Oxide

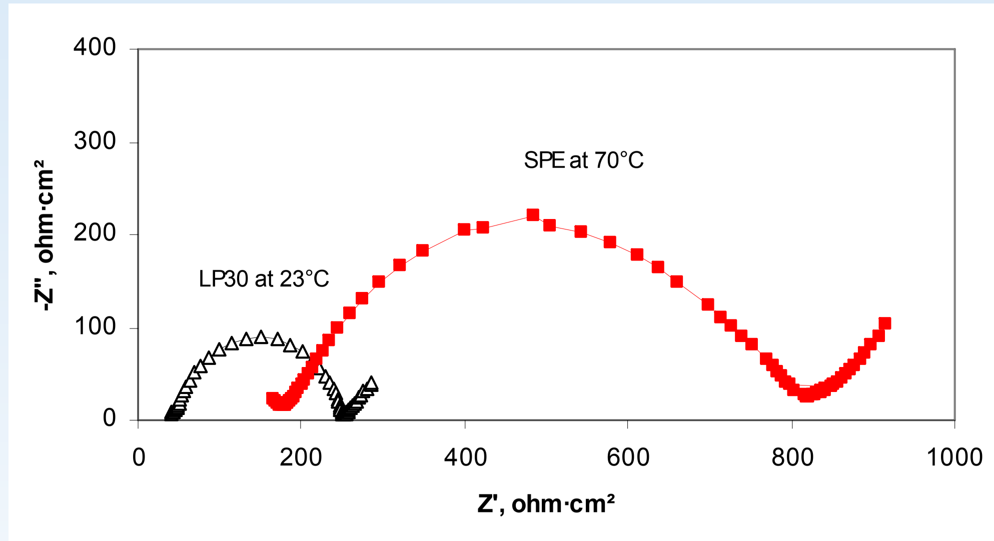
- Vanadium oxide explored at GRC as positive electrode material
- 200 mAh/g (practical capacity for V_6O_{13}).
- 3-Volt, fits stability window
- Preliminary cycle-testing in coin cells with non-optimized electrode formulation.



Preliminary GRC cells built using un-modified PEO as well as rod-coil SPE

Full Cell Impedance

- Cell data at 70°C
- Compare SPE cell with control cell using liquid electrolyte (Merck LP30)
- Higher interfacial impedance with SPE

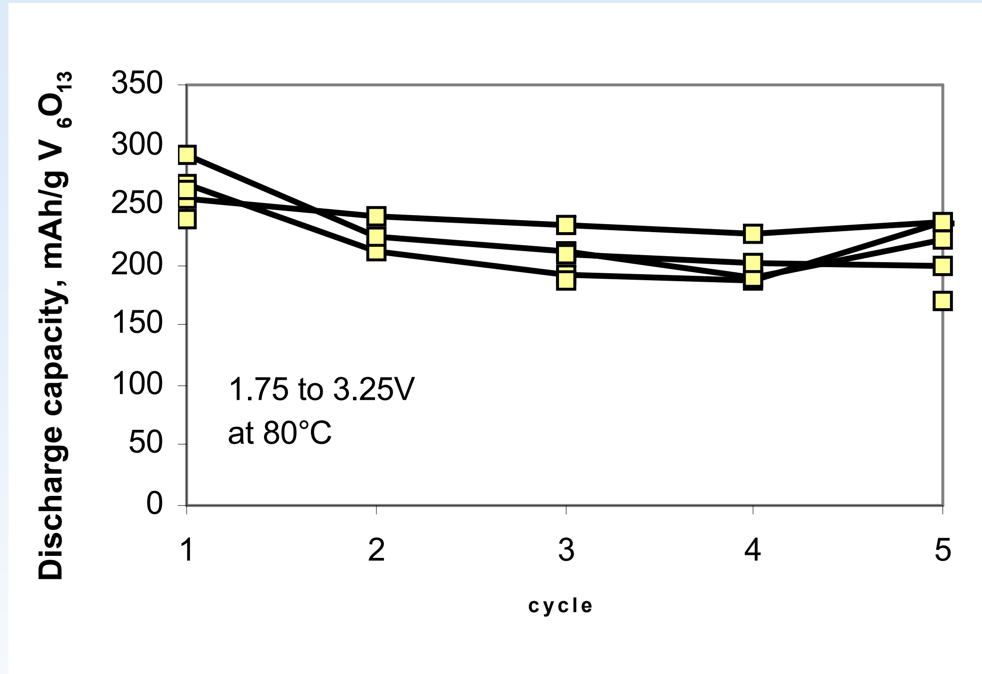


Data for cells before cycling

Even if separator thickness was reduced, interfacial impedance would still be high.

Full Cell Data

- Achieved 200 mAh/g in limited cycling at 80°C, 80μA/cm²
- Variability is due to non-optimized nature of the electrodes



Preliminary lab cells achieved “practical” capacity in limited cycling.

Battery Energy Estimation

With limitations of dry SPEs:

- Cell operates at elevated temperature (80°C)
- 3V cell potential (1 volt less than Li-ion)
- Battery design to accommodate insulation & heaters (adds weight and volume)
- Parasitic power loss to drive heaters

... will a heated battery based on dry SPE have an energy advantage over Li-ion?

Comparison of 30 Ah Prismatic Cells

Chemistry	Li-ion		PERS	
Cell energy, Wh	**108** (at 3.6 V_{avg})		**72** (at 2.4 V_{avg})	
components	grams	wt. fraction	grams	wt. fraction
electrochemical materials	633.1	75.1%	372.9	97.5%
enclosure materials	201.6	23.9%	4.8	1.2%
terminals	1.8	0.2%	1.8	0.5%
auxiliary header materials	6	0.7%	3	0.8%
total weight	842.5		382.5	
Cell specific energy, Wh/kg	**128**		**188**	
cell dimensions, cm.				
overall height	16.71		16.45	
width	8.89		8.75	
thickness	2.27		1.54	
total volume, cm^3	337.3		222.1	
Cell energy density, Wh/dm^3	**321**		**324**	

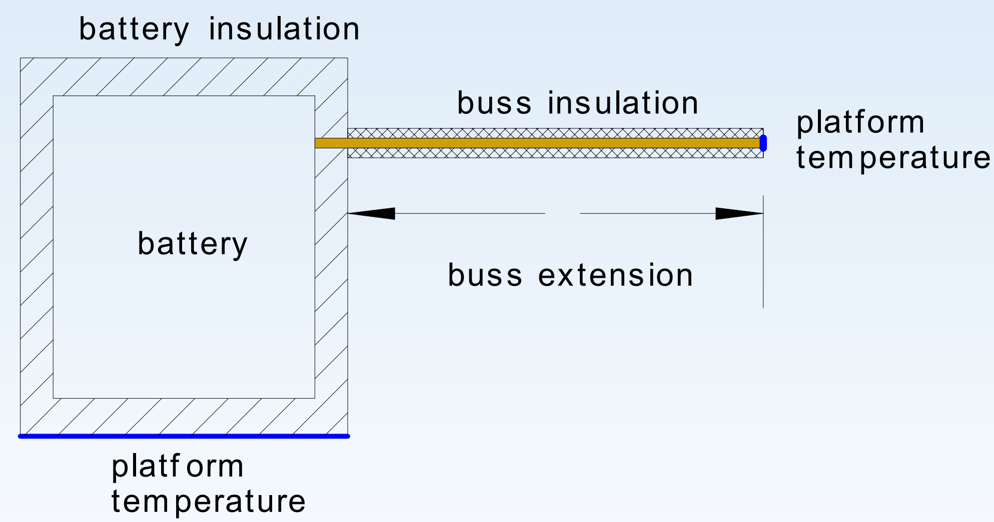
Lower cell voltage is offset by low component weight.
Specific energy is 1.5-times greater at the cell level.

Thermal Model of PERS Battery

Assumptions:

- Uniform cell temperature
- Neglect generation (polarization/entropy)
- Natural convection
- Conduction to platform
- 23°C ambient temperature

Boundary Conditions



Significant heat loss through electrical conductors.

Insulated buss extension is essential, to limit heat flow but but adds weight

Comparison of 28-Volt Batteries

Electrochemistry	Li-ion	PERS	PERS
Allowance for heat loss	none	none	heat loss at 80°C
no. of cells	8	12	12
Specific energy, Wh/kg	**113**	**167**	**146**
Energy density, Wh/dm^3	**269**	**291**	**178**
net capacity, Ah	30	30	27.6*

Even with allowance for parasitic heat loss, PERS battery has significantly greater specific energy.

Insulation reduces energy density.

* 9% of battery power used to run guard-heaters

Cell Electrode Area and Parasitic Weight

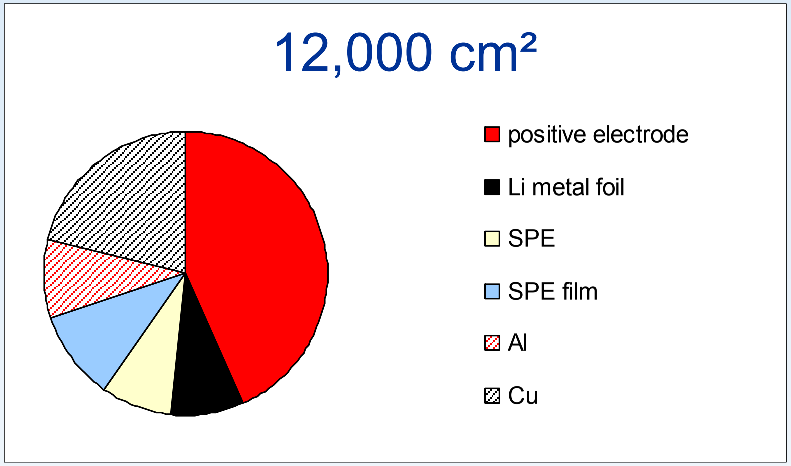
Electrode area is a critical cell-design parameter.
- current density
- active material layer thickness
- relative weight of current collectors

12,000 cm^2 electrode area was selected for the hypothetical 30-Ah cell design:
- 3-mil thick positive electrode active layer
- For C/8 rate (3.75 A) current density is 312 $\mu A/cm^2$
- 30% of the electrochemical material is current collector

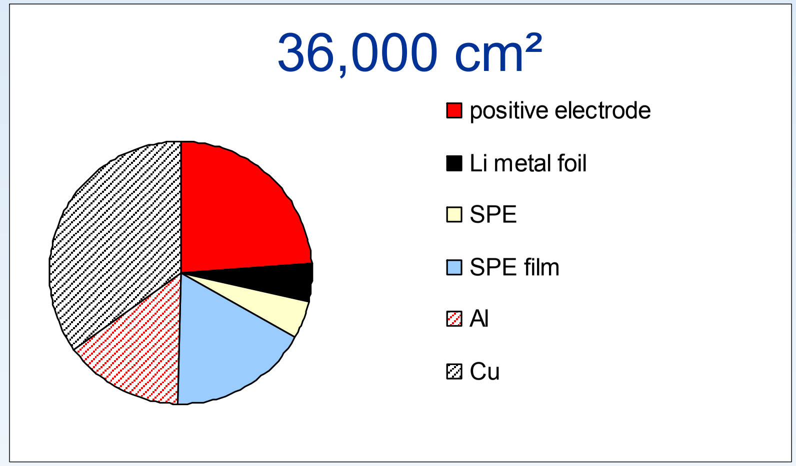
For rates greater than C/8, current density or electrode area must be increased.

What if electrode area is increased by a factor of 3?

Electrode-Area Effect in 30-Ah Cell



cell energy 188 Wh/kg



cell energy 105 Wh/kg

With 3-fold increase in electrode area, half of the cell component weight is occupied by metal substrate.

Assumes “conventional” foil thicknesses 0.8-mil Al & 0.6-mil Cu

Summary

- Over 20 PERS participants helped increase the body of knowledge for novel SPE approaches and produced materials with new characteristics and physical properties.
- Breakthrough-levels of electrochemical performance have yet to be accomplished - work continues.
- A number of SPEs show promise as viable electrolytes at elevated temperature.
- Specific energy advantages are possible for batteries with thermal management systems.
- Cycle-life, utilization, long-term stability, etc. need to be demonstrated in future work with optimized electrodes.

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Acknowledgments

The authors gratefully acknowledge the support provided by NASA and other collaborating governmental agencies

All of the formal NASA PERS Program participants.

The efforts of the participants resulted in a wealth of new and fundamental knowledge into the public domain and scientific literature, which, hopefully, will stimulate more new ideas and approaches to address the challenging criteria for the future viability of the technology.