

Research and Technology Center



BOSCH

October 2, 2009

California Energy Commission
Dockets Office, MS-4
Re: Docket No. 09-ALT-1
1516 Ninth Street
Sacramento, CA 95814-5512

DOCKET 09-ALT-1	
DATE	OCT 02 2009
RECD.	OCT 05 2009

Robert Bosch LLC
4009 Miranda Avenue
Palo Alto, CA 94304
www.bosch.us

Subject: Docket number 09-ALT-1, 2010-2011 Investment Plan

To whom it may concern:

Attached is Bosch's white paper and presentation on high energy battery technology. This was submitted electronically to the docket on Sept. 18, 2009. Thanks,

10/2/09

Jasim Ahmed
Robert Bosch LLC
Research and Technology Center
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Date

High Specific Energy Lithium/Sulfur Cells

ABSTRACT:

This is a proposal to develop high energy lithium sulfur (Li/S) battery technology to enable electric vehicles (EV) with a driving range of 300 miles. Li/S technology offers great potential to meet range demands because of its high theoretical specific energy of 2600 Wh/kg. Such a technology can potentially power all light duty vehicles, and thus reduce annual greenhouse gas emissions (GHG) by 17% and daily oil imports by 9 million barrels.

In addition, Li/S technology possesses advantages in terms of cost, safety, toxicity and abundance. The cost of Li/S cells could potentially be cheaper because of the low cost of sulfur which is in contrast to more expensive materials currently being used in Li-ion cells such as cobalt, nickel or manganese. Material costs contribute significantly to cell cost. Li/S cells can also potentially be safer because of the lack of oxygen which in conventional Li-ion cells reacts with the organic electrolyte to pose safety problems. Other advantages are sulfur's non-toxic nature and the abundance of sulfur in the US with the US possessing 20% of the world's estimated resources.

Current Li/S cells exhibit an excellent specific energy of 350 Wh/kg but suffer from poor cycle life and power capability as compared to conventional Li-ion cells. The ultimate aim of this project is to increase the specific energy of Li/S batteries beyond 600 Wh/kg, increase lifetime to >500 cycles, achieve specific power of >750 W/kg, and meet automotive safety requirements. The key deliverable is a prototype Li/S cell that meets the above requirements.

The goals of the project will be achieved by building on the current work of Prof. Cairns, a pioneer in the field of Li/S cells, and a member of this team. We will accomplish the goals by:

- i) discovering and optimizing new ionic-liquid-containing systems to improve life, ionic conductivity, and thermal stability;
- ii) incorporating the active sulfur into an electronically and ionically conducting structure that accommodates the large (79%) volume change such as a conductive, elastomeric polymer matrix to improve life;
- iii) optimizing the cell geometry and composition to achieve power and energy goals;
- iv) identifying and parameterizing degradation mechanisms to suggest further life enhancement strategies, using diagnostic techniques such as UV/Vis spectrometry.

Currently, our laboratory-scale cells exhibit specific capacities of several hundred to almost 1400 mAh/g-S, and a life of hundreds of cycles. Our calculations show that prototype energy cells can have specific energies in excess of 400 Wh/kg.

We have assembled an outstanding California based team to achieve our goals. **Prof. Cairns (UC, Berkeley)** is a pioneer in the field of Li/S cells, with over 15 years experience in developing Li/S technology. He will be responsible for cell integration. **Dr. Kerr (LBNL)** has extensive experience in the synthesis and development of polymer and non-aqueous electrolytes for use in rechargeable lithium cells and fuel cell membranes. Dr. Kerr will develop new materials such as elastomers that can help improve life. **Bosch** is the world's largest automotive supplier with over 19,000 employees in the US. Its R&D center in Palo Alto, CA has extensive experience in cell characterization, modeling and safety and will be responsible for cell design optimization and characterization.

Long range EVs require safe high specific energy batteries. The proposed investigation of Li/S cell technology will enable us to develop such batteries and our team possesses the required expertise to achieving these goals.

1. Technical Section:

The goal of this project is to deliver safe prototypes of laboratory-scale cells that fulfill the primary EV requirements in specific energy, power and life. The key deliverable is a prototype 600 Wh/kg energy Li/S cell with life of several hundred cycles, pulse power of 750 W/kg and capacity up to 5 Ah.

The primary advantage of Li/S chemistry is its high theoretical specific capacity of 1675 mAh/g which results in a high theoretical specific energy of 2600 Wh/kg. However, the achievable cycle life of Li/S cells has been limited to date. One such life-limiting mechanism involves the process by which sulfur transforms between solid elemental sulfur and lithium sulfide (see Figure 1).

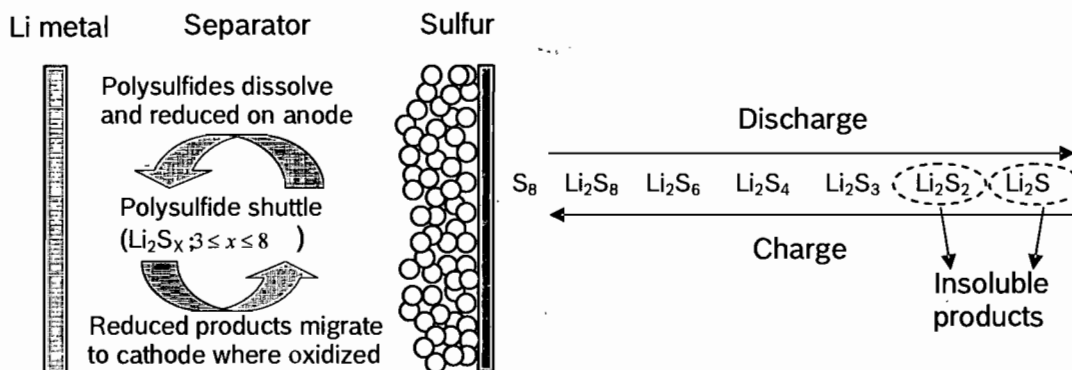


Figure 1: Li/S cell processes

Although elemental sulfur (S₈) and lithium sulfides (Li₂S₂ and Li₂S) are insoluble in electrolyte solutions, lithium polysulfides (Li₂S_x, 3 < x < 8) may dissolve depending upon the electrolyte composition. Such is the case for most conventional organic electrolyte solvent systems used for the Li/S system (*e.g.*, dioxolane-dimethyl ether mixtures). In these systems, soluble polysulfides are free to migrate to the lithium anode and react directly with the lithium. The further reduced polysulfide species produced from this reaction can subsequently migrate to the positive electrode, where they react with polysulfides at a higher oxidation state. Without intervention, this redox shuttle could in principle continue until the sulfur is completely sequestered as immobile and unrecoverable Li₂S at the lithium electrode surface. Even if the redox shuttle mechanism can be inhibited by some protective barrier impermeable to polysulfides between the anode and cathode, the soluble/solid phase-transition nature of the catholyte system may lead to uneven distribution of reaction products, particularly at high currents, which may detrimentally impact the local cathode porosity; excessive stress on the conductive carbon matrix of the cathode during solid precipitation; or isolation of solid products that become fragmented from the conductive matrix.

There are a few approaches to extending cycle life. One approach explored by researchers at Tsinghua University is to immobilize the sulfur in a polymer matrix. Their cells can achieve over 40 cycles but with a specific capacity of only 700 mAh/g. Another approach is to restrict the solubility of the polysulfides by altering the solvent system. Sion Power has been able to achieve a specific energy of 350 Wh/kg and a life of 70 cycles by using proprietary solvents. However, their cycling efficiency is so poor such that at the end of 70 cycles there has been a very significant capacity loss. Researchers from Prof. Cairns group at University of California, Berkeley have done extensive work on solvents to improve performance and life. In 2002, Shim

et al. have shown that the use of a high molecular weight solvent (e.g., triglyme or PEGDME) limits the solubility of polysulfides enabling more than 500 cycles but with a capacity of approximately 200-300 mAh/g.

Currently, our laboratory-scale cells can exhibit specific capacities of several hundred to almost 1400 mAh/g S, and a life of hundreds of cycles. These studies have been performed on swagelok cells, and our calculations show that prototype energy cells can have specific energies in excess of 400 Wh/kg. One of our initial goals will be to build such cells. In Figure 2, we see one embodiment of our cells which shows an initial capacity of approximately 1000 mAh/g S and a significant capacity for the first 10 cycles. Figure 3 shows a more recent embodiment, where we observe a stable capacity at the end of 100 cycles for the case where the mass ratio of PEGDME to ionic liquid is 2.0. The improved performance of these cells over earlier work by Shin et al is due to the addition of an ionic liquid (e.g., $\text{PYR}_{14}\text{TFSI}$) to the above mentioned solvent so as to improve thermal stability, ionic conductivity, and Li-electrolyte interfacial properties. Our investigations show that the sulfur electrode structure is not able to properly accommodate the large volume change of the sulfur during discharge and this limits capacity and life. This will be improved by focusing on structures such as elastomers that can enable such a volume change.

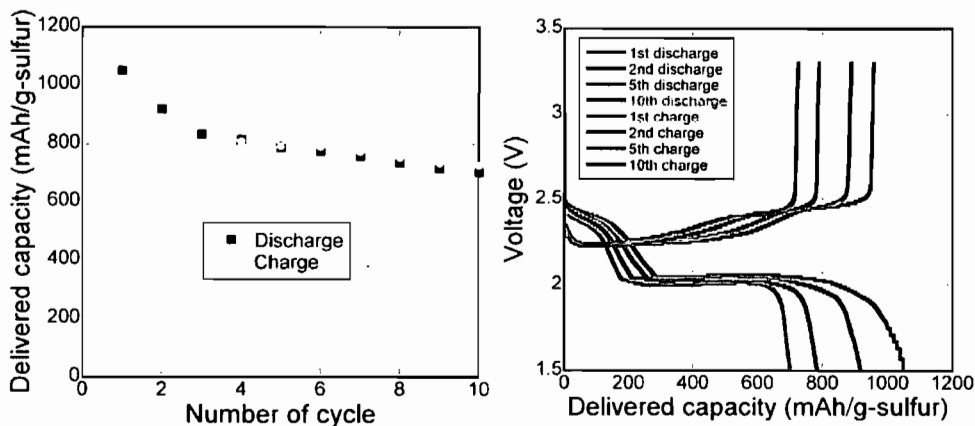


Figure 2: Charge and discharge curves for Li/Ionic Liquid-2M PEGDME-1M LiTFSI/S cells

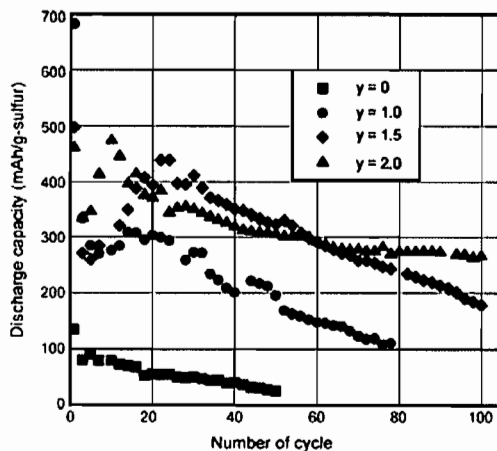


Figure 3: Capacity vs. cycle number plots for several Li/Ionic Liquid-PEGDME-0.5M LiTFSI/S cells with various mass ratios of PEGDME to Ionic Liquid (y)

In this project, the main focus will be on improving performance and life by building on the current work of Prof. Cairns. This project will focus on three main topics:

- 1) the development of new electrode and cell structures such as elastomers that accommodate the large volume change and thus provide for high sulfur utilization and long cycle life
- 2) the development of advanced electrolyte formulations that provide high ionic conductivity, minimum polysulfide solubility, and excellent stability over a range of temperatures and operating conditions; development of electronically and ionically conducting structures such as elastomers
- 3) the optimization of electrode and cell designs through detailed mathematical modeling.

Concurrently, we will build prototype high specific energy cells with capacities up to 5 Ah of existing and our new Li/S concepts. Our calculations show that collectively accomplishing the above tasks will enable us to improve life and meet the specified 600 Wh/kg specific energy target, thereby improving dramatically the prospect for mass commercialization of full-range EVs.

Task 1. Electrode and cell structure development (University of California (UC), Berkeley):

In order to obtain high sulfur utilizations at high rates, with minimal mechanical damage, it is important to have the sulfur in the form of nanoparticles uniformly dispersed within an electronically and ionically conductive matrix, in good contact with a current collector. We will investigate methods for preparing sulfur in nanoparticle form, including colloidal dispersions, and combining it with electronically and ionically conductive elastomers to yield a robust electrode structure that accommodates the significant expansion of the sulfur as it is converted to Li_2S during discharge. Both commercially-available (e.g. ZEON, and duPont elastomers) and LBNL-synthesized elastomers will be evaluated in Li/S cells. Electronically conductive polymers similar to polyaniline will also be evaluated as components for the sulfur electrode, but the goal is a single polymer binder with elastomeric properties, and both ionic and electronic conductivity. New electrode synthesis procedures will be evaluated to incorporate all of the components into the desired arrangement in order to improve cycle life and sulfur utilization.

Task 2. Electrolyte development and synthesis (Lawrence Berkeley National Lab. (LBNL)):

Blends of ionic liquids with PEO and lithium salts have been studied with respect to bulk conductivity issues. However, the interfacial impedance is generally a more serious problem. Our laboratory is presently synthesizing a number of ionic liquids, ionic liquid-like polymers and lithium single ion conductor materials that have adequate bulk transport properties for EV use but possess unacceptable interfacial properties. In addition to ionically conducting polymers, our laboratory is involved in the synthesis and testing of electronically conducting polymers which also contain ionic groups, an example of which is shown in Figure 4. These activities provide a unique capability to investigate the properties required for optimum sulfur utilization. To facilitate investigation we propose to use blends of materials initially to explore the behavior, and once optimum conditions are found we will synthesize the appropriate materials.

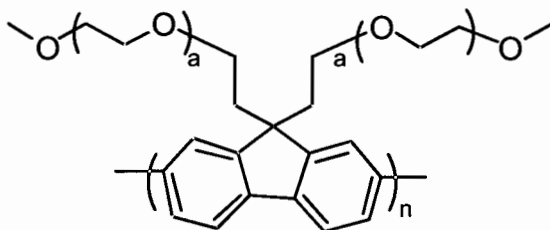


Figure 4: Electronically conducting polyfluorene with ion conducting side chains

Task 3. Design, modeling and characterization of sulfur electrode and Li/S cell (Robert Bosch LLC (Bosch)):

The goal is to develop physics-based models that will be used to understand the performance and cycle life of the sulfur cathode. These models will be used to guide experiments so as to accelerate the development of Li/S cells for the automotive market. We will focus on three areas:

- 1) estimate and minimize particle fracture likelihood so as to improve life;
- 2) particle size optimization for energy, power and stress;
- 3) cell level optimization of energy and power, with targets of 600 Wh/kg and 750 W/kg.

Modelers will interact closely with experimentalists at UC Berkeley and LBNL to parameterize and validate models. Furthermore, Bosch will perform cell characterization experiments, together with UC Berkeley, to analyze and improve performance and life.

We aim to estimate the likelihood of particle fracture as a function of particle size, rate of charge and discharge, and electrode design by modeling the stress generation due to lithium insertion and extraction. In an immobilized sulfur cathode, the active material expands upon lithium insertion by 79%, and such a change could result in fracturing of the sulfur particles which could decrease life. At Bosch, we have developed models that account for extreme volume change. For instance, we have shown that current distribution can have a profound effect on the maximum stress generated, even at the low rates typical of a high-energy cell (see Figure 5), and we aim to develop such models so to minimize fracture likelihood.

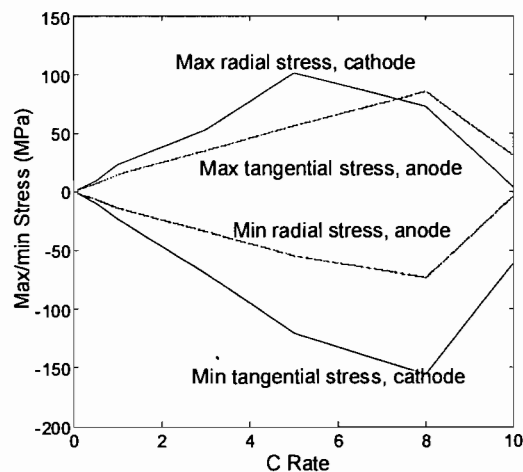


Figure 5. Maximum stress generated during discharge of an energy cell (i.e., with nominal electrode thickness of 200 μm).

In addition, we will focus on particle size and cell performance optimization. As particle size decreases, there is improved rate capability and reduced stress but side reactions, such as limited polysulfide dissolution, increase, and a larger weight fraction of inactive material is required to provide uniform electronic conduction, particle adhesion, and immobilization. By way of example, Figure 6 shows the computed weight fraction of active sulfur in a composite cathode as a function of particle size, assuming a minimum thickness of 2 nm for the immobilization layer. It is clear that a higher weight fraction, which implies a higher cell specific energy, increases with particle size. We will develop relations, empirically and via mathematical models, to select the best particle size for the system. In the area of cell optimization, we will optimize design parameters such as porosity, electrode and current collector thickness, and materials selection to

meet energy and power requirements. In addition, we will account for manufacturing and materials costs, safety requirements, and cycle life requirements.

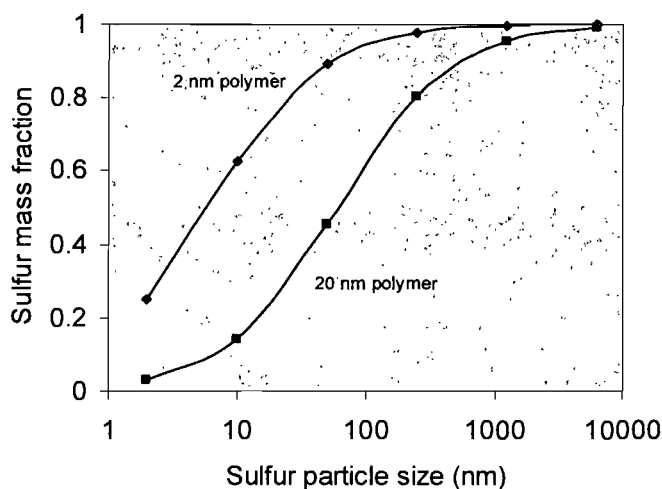


Figure 6. Mass fraction of sulfur in an electrode with sulfur particles covered by elastic immobilization polymers, as a function of sulfur particle size and polymer thickness.

2. Mission Impact Section:

2.1 Technology impact:

Mass commercialization of EVs with ranges greater than 300 miles will require batteries with high specific energy. As Figure 7, shows, a specific energy of 575 Wh/kg on a cell basis is required for an EV to reach 300 miles on a single charge (under the assumption of a 200 kg battery limit). Today's Li-ion cells with specific energies at approximately 200 Wh/kg can only enable vehicles with limited ranges of approximately 120 miles. Significant improvements in cell specific energy are required for vehicles to cross the 300 mile barrier and to match the current range of vehicles. It can also be seen from Figure 7, that traditional Li-ion chemistries need to develop dramatically in order to meet EV range requirements; a doubling of their current specific energy would not be enough. A doubling of the specific energy which is the long-term goal of the DOE represents in all likelihood the maximum achievable for Li-ion chemistries. To reach energies greater than 575 Wh/kg requires new chemistries such as Li/S, which is the focus of this project. The goal is to have a Li/S cell with 600 Wh/kg so as to enable EVs with ranges in excess of 300 miles.

Today's Li-ion cells at 200 Wh/kg are at approximately 33% of their theoretical specific energy, while Li/S cells at 350 Wh/kg are at 14%. Further development of Li/S cells to the same limits as Li-ion cells would put Li/S cells at 866 Wh/kg which would enable EVs to exceed 450 miles on a single charge. Thus, further investigation of Li/S cells is required and is the goal of this project.

Li/S technology possesses other advantages in terms of cost, toxicity, safety and abundance. Lithium/sulfur cells could potentially be inexpensive because of the low cost of sulfur at \$0.25/lb. This is in comparison to the price of cobalt at \$19/lb or manganese at \$1/lb or nickel at \$5/lb, all of which are used in current Li-ion cells and contribute significantly to the cell cost. Other advantages are sulfur's non-toxic nature, the technology's potential to be safer because of its lack

of oxygen, and the abundance of sulfur with the US possessing 20% of the world's estimated resources.

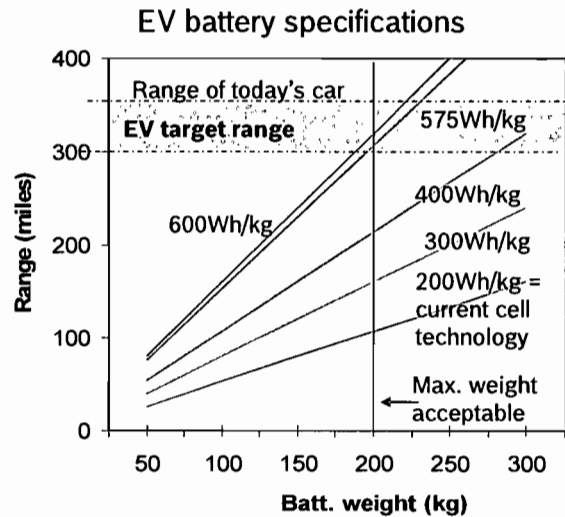


Figure 7: EV battery specifications

Thus, Li/S cell technology has the potential to transform the energy landscape of the US. Li/S cells, because of their high energy content, could power all light duty vehicles, displacing petroleum as the source of energy. Currently, light duty vehicles account for approximately 17% of greenhouse gases (GHG) emissions. Li/S batteries could potentially reduce GHG emissions from this sector to zero (assuming renewable sources of electricity). Furthermore, the light duty vehicle market accounts for approximately 9 million barrels of oil every day, of which over 3 million barrels come from the Persian Gulf and Venezuela. Li/S technology can potentially displace all 9 million barrels and thus remove our dependence from the above-mentioned countries.

Li/S technology has tremendous market potential. At the current rate of 15 million new vehicles being sold annually in the U.S., an average battery size of 40 KWh, and at the DOE long-term cost target of \$100/kWh, the total market for Li/S technology is \$60 billion per year in the U.S. alone. Other potential applications include the PDA, laptop, and cell phone markets where the Li/S battery's high specific and volumetric energy densities pose a great advantage. Future applications could include the still nascent stationary storage market. Thus, a successful introduction of this technology could completely transform the energy storage market, and enable the US to be the world leader. It will lead to the creation of thousands of green jobs in cell and battery manufacturing, electrode material production, electrolyte production, separator manufacturing, marketing, and sales positions.

2.2 Team, transition strategy, and facilities

Prof. Cairns of University of California, Berkeley is a leading battery expert, with more than 15 years of experience in high energy Li/S technology. Prof. Cairns will lead the Li/S cell development working closely with Dr. Kerr of Lawrence Berkeley National Lab (LBNL) and Robert Bosch LLC (Bosch). Dr. Kerr, an expert in polymers will help design and synthesize new

cathode binders, elastomers, and structures required to improve performance and life. Bosch is the largest automotive equipment supplier in the world with over 19,000 employees in the US. Its Research and Technology Center located in Palo Alto, CA will lead its Li/S efforts and will bring its experience in cell design, modeling and characterization to accelerate the development of Li/S cells. The majority of the results of our work will be made publicly available in terms of publications in conferences and peer-reviewed journals.

The successful completion of this project will ensure that the key technological hurdles are solved. However, further development is required to bring these cells to the market. These cells will have to undergo rigorous automotive testing to ensure 1) that performance requirements over a wide range of operating conditions are met, 2) that they are safe, and 3) that they meet reliability and quality standards. In this project, Bosch will use its expertise in the automotive field to test promising cell designs under suitable automotive conditions so as to accelerate the development of promising Li/S cell concepts. Bosch is committed to commercializing Li/S technology.

Available facilities include 3 glove boxes; electrode preparation and cell assembly equipment; >180 battery test channels; >10 impedance (EIS) channels; environmental chambers; a 392-core Xeon computing cluster (4.46 TFLOPs); a 3 Schlenk-line synthetic chemistry lab; and extensive materials characterization equipment such as viscometer, Karl-Fischer titrator, DMA, DSC, TGA, FTIR, UV/Vis, slow CV, HPLC, GC-MS, ICP-MS, and Capillary Electrophoresis analyzers. We have access to NMR (through the Molecular Foundry), Jeol SEM, AFM, and SAXS (at the Atomic Light Source).

Safer High Energy Batteries

Safer High Energy Batteries

University of California, Berkeley
Lawrence Berkeley National Lab. (LBNL)
Bosch Research and Technology Center (Palo Alto)

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Safer High Energy Batteries

Summary

- ⇒ Investigate high energy safe Lithium Sulfur (LiS) battery technology to enable > 300 mile range EVs

LiS battery technology	Li-ion battery technology
⇒ High specific energy: >600 Wh/kg achievable	⇒ Maximal achievable specific energy ~400 Wh/kg
⇒ Potentially inexpensive	⇒ Expensive
⇒ Safer	⇒ Safety concerns

- ⇒ World-class California-based consortium formed to develop LiS batteries
 - Prof. Cairns of UC Berkeley
 - Dr. Kerr of LBNL
 - Bosch Research and Technology Center (RTC) in Palo Alto

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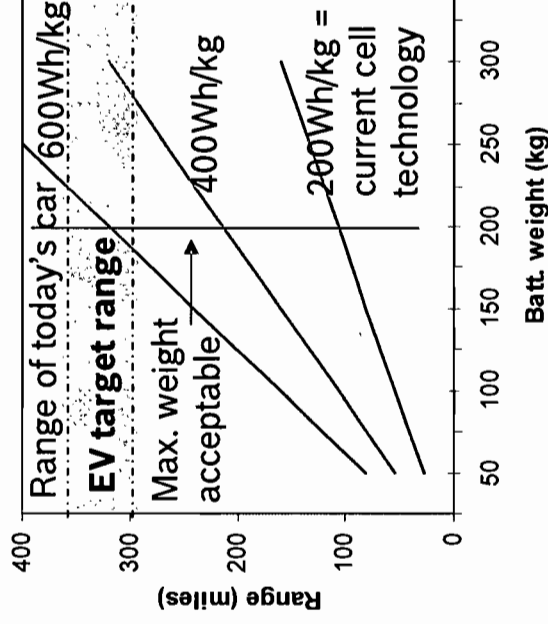
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Safer High Energy Batteries

EV battery technology requirements

- For long EV driving ranges of 300 miles, high specific energy (~600 Wh/kg) batteries are needed
 - However, safety for EVs becomes of critical importance because of large battery pack (> 20KWh)
 - By 2015, 2.5M vehicles with Li battery technology
 - Need safe materials, safe cell designs
 - Life > 10 years and > 1000 cycles is challenging
 - **Development of safe long-lasting battery cell technology is needed to enable long range EVs**
- EV battery specifications



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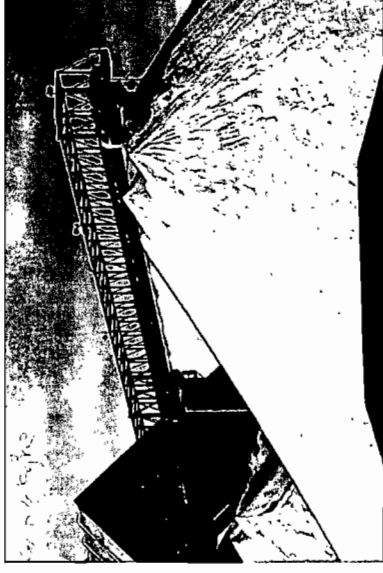
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Safer High Energy Batteries

High energy safe LiS battery technology

- ⇒ High theoretical specific energy of 2600 Wh/kg (1675 mAh/g)
- ⇒ Inexpensive: \$0.26/lb (CoO₂ \$19/lb)
- ⇒ Non toxic
- ⇒ Safer → no oxygen
- ⇒ Plentiful
- ⇒ Key challenge: Improving cycle life

Sulfur byproduct from HCs



- ⇒ **Project goal:**
 - **Development of high cycle life safe LiS technology to enable long range EVs > 300 miles**

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California partnership to develop LiS batteries

- ⇒ World class CA-based partnership formed to develop LiS batteries
 - Dr. Kerr of LBNL: leading expert in polymers and materials
 - Prof. Cairns of UC Berkeley: world leading LiS researcher
 - Bosch Research and Technology Center (RTC) in Palo Alto: cell modeling & characterization expertise

Partners/topics

LBNL:
Materials/polymers

UC, Berkeley:
LiS cell development

Bosch RTC (Palo Alto):
Modeling, characterization

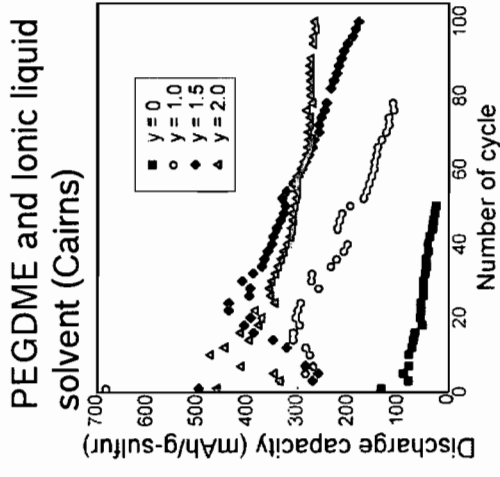
**Safe long-life
LiS battery**



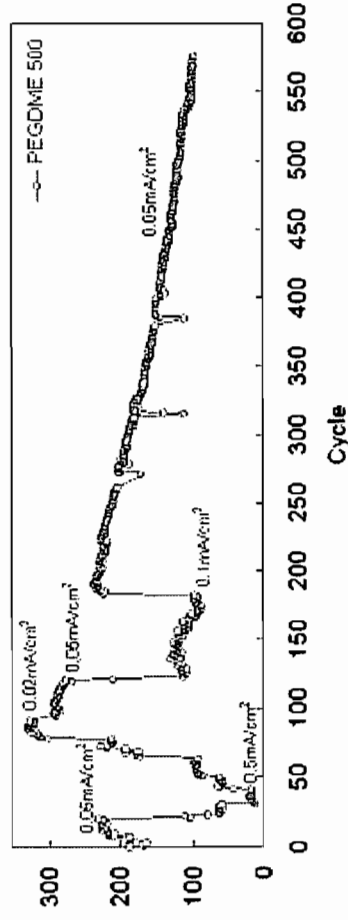
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Prof. Cairns of UC Berkeley

→ Prof. Cairns (UC Berkeley): over 10 years experience in LiS technology



Use of PEGDME solvent (Cairns)



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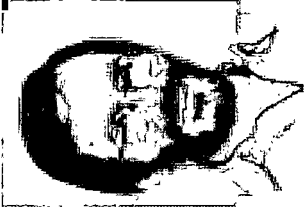


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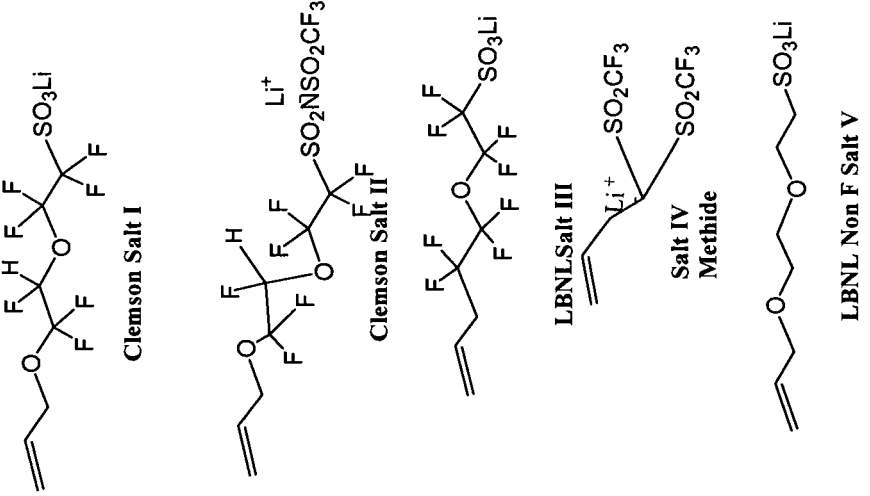
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Dr. Kerr of LBNL

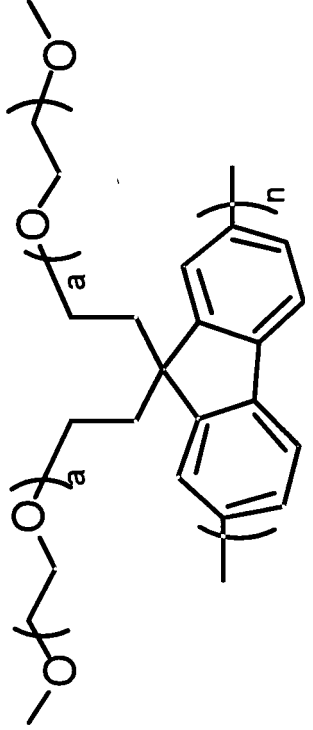
- Dr. John Kerr (LBNL):
 - polymer and electrolyte expert



PEP(EO)x-based Ionomers



Electronically conducting polyfluorene with ion conducting side chains



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Safer High Energy Batteries

A diversified technology company – green Bosch



Bosch Group
Sales: 62+ bn USD*
Associates: 272,000+

Automotive Technology Sales: 38.9 bn USD
Industrial Technology Sales: 8.2 bn USD
Consumer Goods, Building Technology Sales: 16 bn USD

ersol
Bosch Group

SB LiMotive
A joint company of Samsung and Bosch



By 2020, Bosch plans to cut emissions by at least 20% from 2007 level.

Franz Fehrenbach,
CEO Bosch Group
3/25/2009



* EUR to USD conversion

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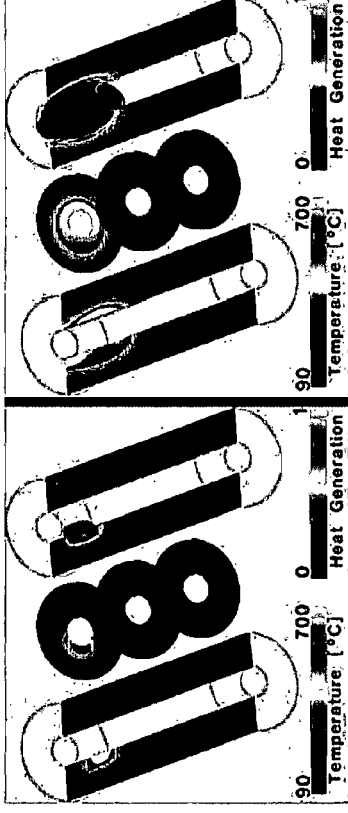
Bosch in CA

- Over 650 employees in CA (19,000 in US)
- Divisions present in CA
 - Power tools, home appliances
 - Solar energy (in Camarillo)
 - Automotive
 - Research and Technology Center (RTC) in Palo Alto, CA
- Bosch RTC battery expertise
 - Modeling
 - Performance optimization
 - Aging analysis
 - Safety

Bosch RTC in Palo Alto, CA



Heat propagation: internal short present



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