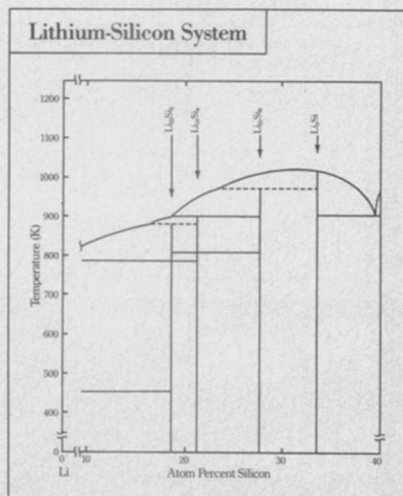


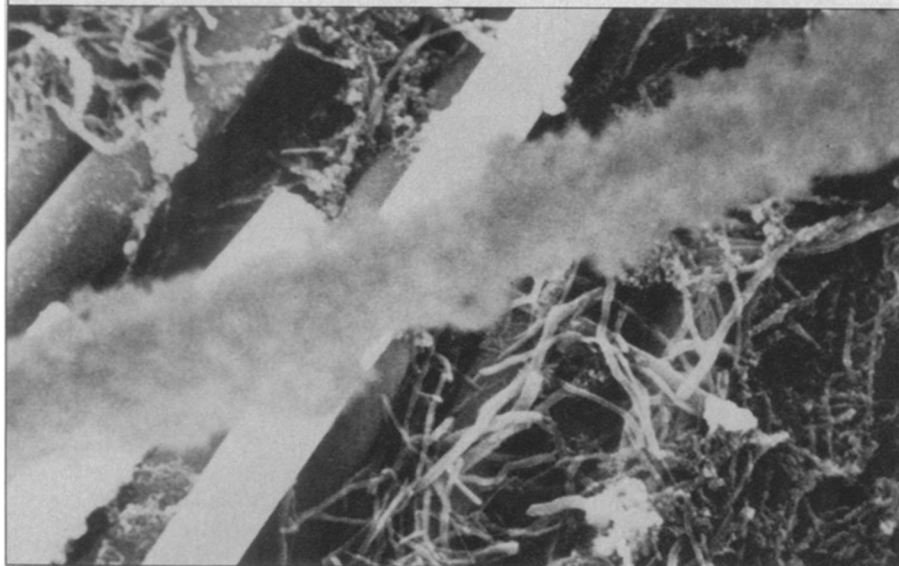
The Lithium Paradigm

The practicality of a mass-produced electric car depends upon the development of a long-life, low-cost, rechargeable battery. Recent discoveries at the General Motors Research Laboratories have encouraged scientists seeking to harness the abundant but elusive energy available in lithium—a highly desirable battery component.



Partial phase diagram of the lithium-silicon system. Lithium activity changes by two orders of magnitude in the concentration range shown.

Color-enhanced scanning electron micrograph showing the results of lithium attack on boron nitride.



HIGH ELECTROPOSITIVITY and low equivalent weight make lithium an ideal battery reactant, capable of supplying the specific energy needed to operate an electric vehicle. The source of the abundant energy available in lithium, however, is exactly what makes it almost impossible to manage. The challenge is to prepare alloys and find materials stable enough to contain the aggressiveness of lithium without greatly suppressing its activity.

New knowledge of the thermodynamic properties of lithium-containing materials has been revealed by fundamental studies conducted at the General Motors Research Laboratories. Investigations, carried out by Dr. Ram Sharma and his colleagues, aim at developing a basic comprehensive

understanding of selected "exotic" systems. Their work is directly related to the search for an advanced molten salt battery cell.

Specific energies greater than 180 W·h/kg, about five times that of the lead-acid battery, have been demonstrated by electrochemical cells utilizing LiCl-KCl electrolyte and electrodes of metal sulfide and lithium alloy. But operating temperatures of 723 K and the aggressive nature of the chemical reactants pose serious new challenges to cell construction materials. Of particular concern is the lithium attack upon separators and seal components. Most inorganic insulators, including the refractory oxides and nitrides, are destroyed or rendered conductive by this attack. Boron nitride, one of the more resistant materials, has been the subject of Dr. Sharma's recent, successful efforts to establish conditions under which attack may be avoided.

Dr. Sharma began by exploring the thermodynamics of the lithium-silicon system. Silicon reduces the activity of lithium without substantially increasing its weight, and produces a manageable solid at 723 K.

Constant-current potentiometry experiments were carried out in an inert atmosphere. The electrochemical cell consisted of a Li-Si alloy positive electrode, a eutectic mixture of LiCl-KCl electrolyte, and two Li-Al alloy electrodes—one negative and one reference electrode.

A series of anodic and cathodic cycles at very low current densities indicated three well-defined voltage plateaus below 80 atom percent lithium composition. This behavior was confirmed by experiments in which pure silicon was used in place of Li-Si alloy as the starting material.

The results were used to modify the Li-Si phase diagram, which indicated only two such plateaus. The revised phase diagram shows four compounds: Li_2Si , $\text{Li}_{21}\text{Si}_8$, $\text{Li}_{15}\text{Si}_4$ and $\text{Li}_{22}\text{Si}_5$. The exact composition of $\text{Li}_{21}\text{Si}_8$ had not previously been known.

Dr. Sharma confirmed the existence of the new compound by x-ray diffraction analysis. He determined its melting point to be 976 ± 8 K by differential thermal analysis. He produced a scanning electron micrograph that clearly indicates a single phase for the compound. He was also able to determine the maximum nonstoichiometric ranges of the lithium-silicon compounds from charge passed during the transitions between voltage plateaus.

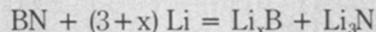
KNOWLEDGE OF THE lithium activity present in the system's various compounds allowed Dr. Sharma to evaluate the stability of boron nitride with Li-Si alloys of differing composition.

A controlled potential was imposed on a boron nitride cloth sample in an electrochemical cell.

By monitoring the current in the cell at different potentials, Dr. Sharma established the point at which lithium activity produces reaction.

Boron nitride was found to react with $\text{Li}_{15}\text{Si}_4$ only when in the presence of $\text{Li}_{22}\text{Si}_5$. The new compound, $\text{Li}_{21}\text{Si}_8$, did not exhibit sufficient lithium activity to attack boron nitride.

Reaction occurred according to the following equation:



The lithium nitride that formed during reaction dissolved in the molten salt electrolyte, but the lithium boride remained on the surface and became electronically conductive, causing high self-discharge in the cell.

"The establishment of the region of stability of boron nitride makes it possible to recommend appropriate charging limits," according to Dr. Sharma.

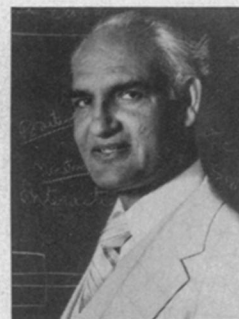
"Restricting the amount of charge in keeping with the recommended limits will control lithium activity, preventing the formation of highly-conductive compounds and adding durability to an electrochemical system which already displays high specific energy. Ultimately, that brings the prospect of high-performance electric vehicles closer to reality."

THE MAN BEHIND THE WORK

Dr. Ram Sharma is a Senior Research Scientist in the Department of Electrochemistry at the General Motors Research Laboratories.

Dr. Sharma was educated in India and England. He graduated from Banaras Hindu University with an M. Sc. in physical chemistry. He received a Ph. D. in physical chemistry and chemical metallurgy from London University's Imperial College of Science and Technology.

Before joining General Motors in 1970, Dr. Sharma conducted research at the Argonne National Laboratory, the Institute of Direct Energy Conversion at the University of Pennsylvania, the Nuffield Research Group in England and the National Metallurgical Laboratory in India.



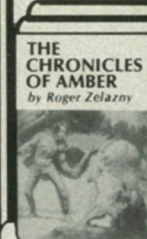
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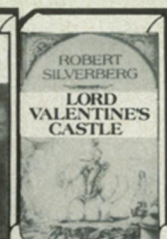
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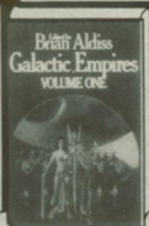
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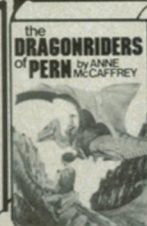
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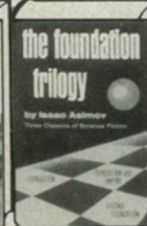
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