

Batteries - Yesterday, Today and Tomorrow

Robert A. Huggins

Professor of Materials Science, Emeritus

Stanford University

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But first:

Three relevant quotes from Thomas Edison

Just as soon as a man gets working on the secondary battery it brings out his latent capacity for lying.

Scientifically, storage is all right, but, commercially, as absolute a failure as one can imagine.

"The storage battery is, in my opinion, a catchpenny, a sensation, a mechanism for swindling the public by stock companies.

And my favorite:

**Making predictions can be rather precarious,
especially when they have to do with the future.**

I shall talk about the evolution of some electrochemical energy storage technologies, where it has gone, and a few comments on where it may be going in the future

But first:

Why can't batteries be improved like semiconductors, where they seem to follow Moore's law, with continually more devices per unit surface area ?

The problem is that electrical charge is stored in ions, which have a finite size. This limits the maximum amount of charge that can be stored per unit volume

Progress in this area has not been linear.
Some important changes have come from surprises.

A bit of history:

Some archeologists claim that there is evidence that the Egyptians had an elemental battery,

But the battery community generally thinks that this technology started with Volta's Zinc / Silver cell in Italy in 1800

The Lead / Acid cell used in your auto was invented by Plantè in France in 1859

Real changes have only come recently

Edison invented the Iron / Nickel battery in 1901

It was used as the power source for early electric autos

The Cd / Ni (or NiCad) cell was developed and used
in German aircraft during WW II

This was uncovered by the Allies after the war, and
brought to the US in 1946

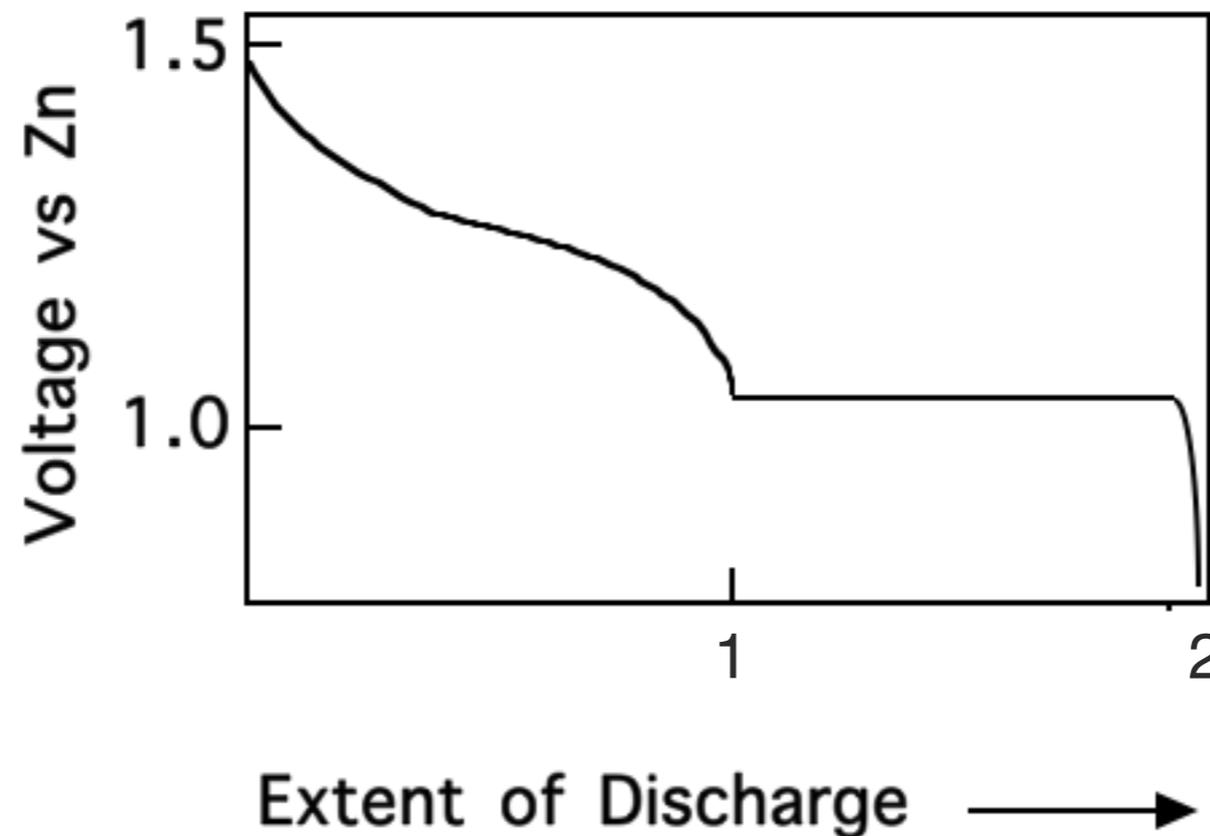
Co-incidence: I did an undergraduate thesis on
sintering the nickel electrode in the Physics
Department of Amherst College in 1950

Zn / MnO₂ “alkaline” batteries

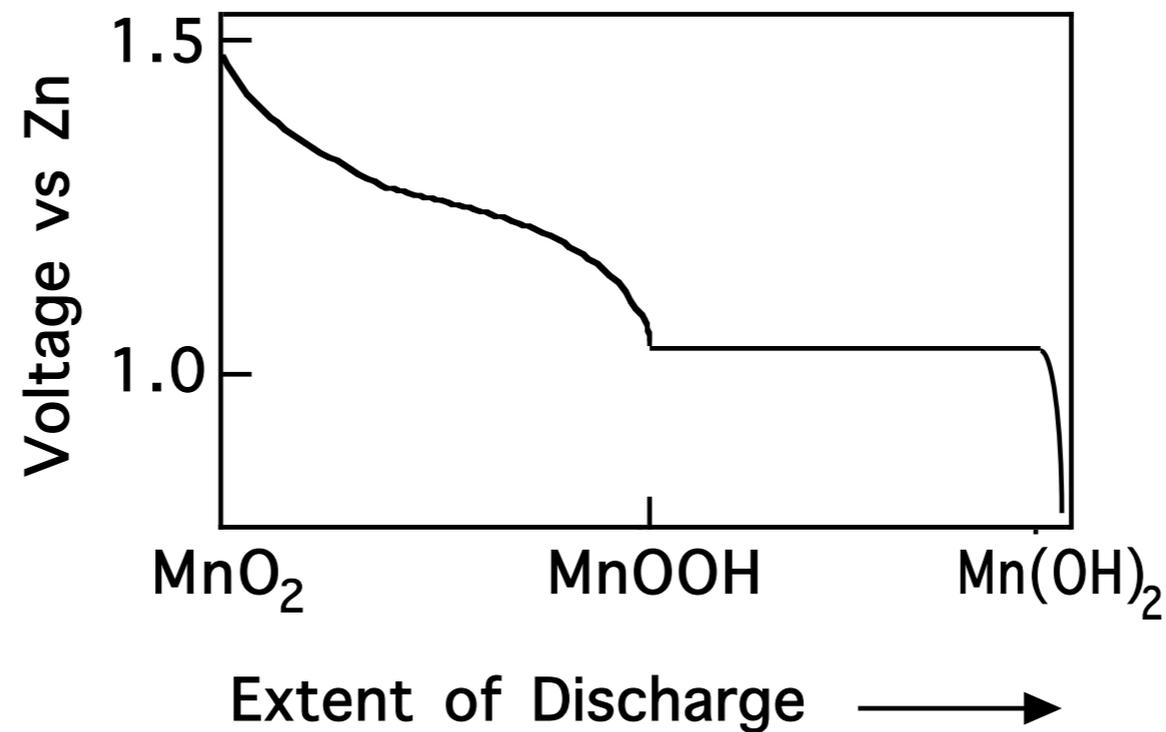
Development started in 1950s

These are “primary”, i.e. not - rechargeable cells

The voltage drops as they are discharged



In 1984 it was shown that the reaction actually involves hydrogen insertion into the solid MnO_2 electrode. Zinc is only indirectly involved.



The energy stored is the area under the discharge curve

Most of these cells are used for applications that require over 1.2 V, so about half of the energy is not used

Metal hydride / Ni batteries

First work by Daimler Benz in Germany on the use of simple AB₂ type metal hydrides for auto starter batteries, starting in 1967

Work was stopped

The kinetics were not satisfactory, and they were too expensive for use in autos

The rapid reaction of hydrogen with the AB₅ family of alloys was discovered by accident in 1970

They were being studied for their magnetic properties in the Philips Laboratories in the Netherlands

Solid samples were annealed at high temperatures overnight, and kept in a hydrogen atmosphere to avoid oxidation

In the morning they were found to have turned into a pile of powder.

This caused Philips to start investigating the reaction of hydrogen with this family of alloys to form metal hydrides for several applications

But the development of the use of these hydrogen
- containing alloys as battery electrodes was
pursued much more vigorously in both the United
States and Japan

First work in the US was by Ovonic
Battery near Detroit. This became
commercial in 1989

Patent fights between Ovonic and the
Japanese companies in the US

Final compromise was a symbolic license fee
paid by the Japanese

Japanese development was centered in GIRIO,
(Government - Industrial Research Laboratory - Osaka)
starting in 1975

Companies sent their employees to work there temporarily;
they transferred basic technology and knowhow
when they went back to their companies

World production is now dominated by Japanese firms:

Sanyo, Matsushita, Yuasa, Hitachi, Sony, etc.
and Ovonic is bankrupt

In the US, the Department of Energy sponsored research on metal hydrides in my lab at Stanford, as well as elsewhere

But like all other battery research in the United States, it was turned off during the Reagan administration

Metal hydride batteries are now very reliable,
with long cycle lives

They are used in the Toyota Prius, for example

They use rare earth elements in the metal
hydride negative electrode

The common example is the lanthanum
nickel alloy, LaNi_5

This type of battery also operates by the (reversible) insertion of hydrogen ions into the negative electrode material, the rare earth alloy in this case



Rare earth alloys also play important roles in many technologies due to their special magnetic and optical properties

There is growing concern about the future availability of these materials, especially in Japan and the US, for the world rare earth market is now dominated by China

Except for the traditional Pb - acid cells and the high temperature solid electrolyte systems that will be discussed later, all current battery systems have solid electrodes in which ions enter and leave from a liquid electrolyte

Thus the real action is inside the solid electrodes, not on their surfaces

The reactions inside the solid electrodes determine their potentials, and thus the battery voltage

The solubility limits of species in the solid electrodes determine the capacity of the system

Electrochemistry is traditionally primarily concerned with:

the properties of ions in liquid electrolytes

**ionic / electronic interactions on the
surfaces of solid electrodes**

**But the main themes in modern battery development
do not appear in textbooks on electrochemistry**

Instead, the central ideas, and the leading people,
now mostly come from other disciplines

Solid state scientists, materials scientists
and solid state chemists have taken over the
leadership from conventional
electrochemists

Physicists have played a minor role

A major innovation that came from the solid state science community has resulted in solid electrolyte cells

All the traditional battery systems are of the S / L / S type, with solid electrodes physically separated by a liquid electrolyte

But why not a L / S / L system, with a solid electrolyte separating liquid electrodes ?

The Na/S high temperature battery was invented in the Ford Motor company lab in 1967

It involves the use of the sodium in the beta form of Al_2O_3 ($\text{Na}_x\text{Al}_2\text{O}_3$) that has a layer-type crystal structure. Experiments showed surprisingly high sodium ionic conductivity at specific compositions.

This ceramic material is a fast ionic conductor and an electronic insulator - thus it can be used as a solid electrolyte

Liquid Na / solid electrolyte / Liquid Sulfur

This is a L / S / L system, with a solid Na^+ - conducting electrolyte separating liquid electrodes

Henry Ford, Jr. was upset when heard about this discovery in his laboratory, for it might lead to practical electric autos, which he did not want.

He fired the Director of Research and told the inventors, Joe Kummer and Neal Weber, to stop work on it, and to work on catalysts instead

Further research and development on the Na/S battery occurred in Europe and Japan, instead of in the US

The only commercial source now is NGK in Japan

This happened shortly after I returned to Stanford from a sabbatical leave in Germany - where I had been studying scientific aspects of ionic transport in solids

We were the first university research group in the US to begin working on solid electrolytes, and their use in batteries

Then came another surprise,
this time from South Africa

The Na/NiCl₂ “Zebra” Battery

Analogous to the the Na/S battery

Liquid Na / solid electrolyte / liquid NaAlCl₄ plus solid NiCl₂

After being developed in secret in South Africa, this system first became public in the US in 1986, after normal political relations were re-established between the two countries

This configuration is now called the “Zebra battery”, although this name originally stood for “Zeolite Battery Research Africa”, something quite different.

Zebras are symbolic of South Africa

Both the Na / S and the Na / NiCl₂ batteries operate at elevated temperatures, 300 to 400 C

They were being considered for electric autos in Europe

When I was Chief Scientist at the Center for Solar Energy and Hydrogen Research in Germany, we did some safety testing in 1994 for the European auto manufacturers

The violent results led to the rapid abandonment of the development of that type of battery for use in vehicles in Europe

Development efforts on high temperature batteries using beta alumina as a solid electrolyte continued in Japan, but they were aimed at relatively safe stationary storage applications.

NGK is now the only source of Na/S solid electrolyte batteries in the world

These are being used in the US to help alleviate transients in the large scale electrical grid

What about Lithium - ion cells ?

Work in this area started with the Solid State Ionics Conference in Belgirate, Italy in 1972

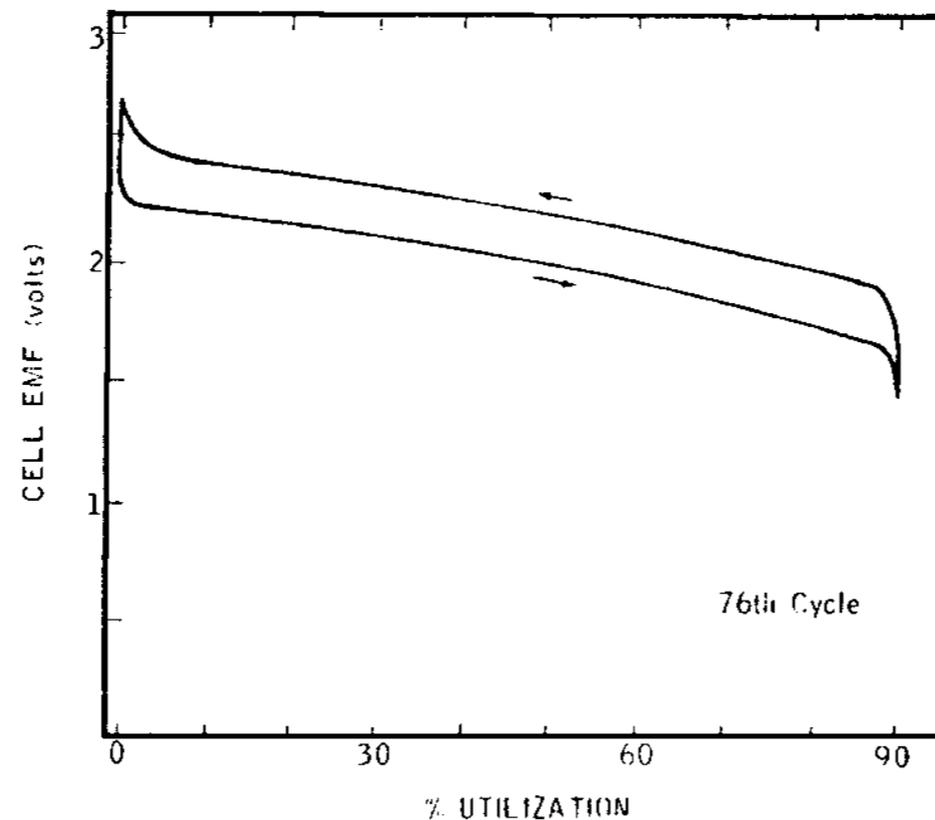
Stan Whittingham and Michel Armand, both postdocs in my lab, and I showed that lithium ions can move very rapidly into solids with appropriate crystal structures

Thus they can be used as solid electrodes in lithium batteries

After leaving my lab, Stan Whittingham got a research position at the Exxon laboratories

Others there were interested in superconductivity, and had been studying a family of sulfides with layer-type crystal structures for that purpose

He began investigating the insertion of lithium ions into these sulfides, and quickly found out that this can happen very fast and reversibly, particularly in TiS_2 in 1976



Exxon's Li/TiS₂ battery was the first example of a useful lithium - ion battery

But Exxon's management decided to not go into the battery business, and this activity was discontinued in the US

Two important discoveries

Work in the Inorganic Chemistry Laboratory in Oxford (from which I had a series of 5 postdocs) in 1980 showed that it is possible to reversibly remove lithium from some layer-structure oxides, LiCoO_2 and LiNiO_2 in 1980

It was shown, both in Grenoble, France and in Bell Labs, that lithium can be added reversibly into the layer structure of graphite in 1981

Bell Labs ended up with the patent, and later made many millions of dollars from it.

These were both opposite of the then-current lithium
battery development directions,

in which lithium was added to positive electrode
materials

and lithium was deleted from negative
electrode materials
during discharge

So nothing much happened in the US or Europe

The era of commercial lithium - ion batteries actually began when Sony put those two electrodes together, and started to produce and sell camcorders with lithium batteries in 1990.

This was a big surprise

Also, contrary to prior practice, these cells were assembled in the discharged state, rather than the charged state.

There has been gradual improvement in their properties since that time

There is a lot of current work on various versions of Lithium - Ion batteries

This involves a large amount of US government money

Most of this effort is aimed at the potential market for their use for vehicle propulsion, as well as portable electronics

Work is being done to increase energy storage by using oxide positive electrodes with higher potentials to increase the cell voltage

Work also being done on liquid organic electrolytes that are stable to higher voltages

There is a search for negative electrodes with higher capacities and better cycle life than graphite

One approach is the use of lithium nanowires

This originated from work by Candace Chan at Stanford

But there is a lot of concern about the price, which is about 80% determined by materials costs, and safety issues

The price is particularly important in connection with the introduction of the use of this type of battery into automobiles

But there is also a serious safety problem

There have been a number of cases in which small lithium-ion cells have caught on fire

This could also happen with larger applications, such as vehicles

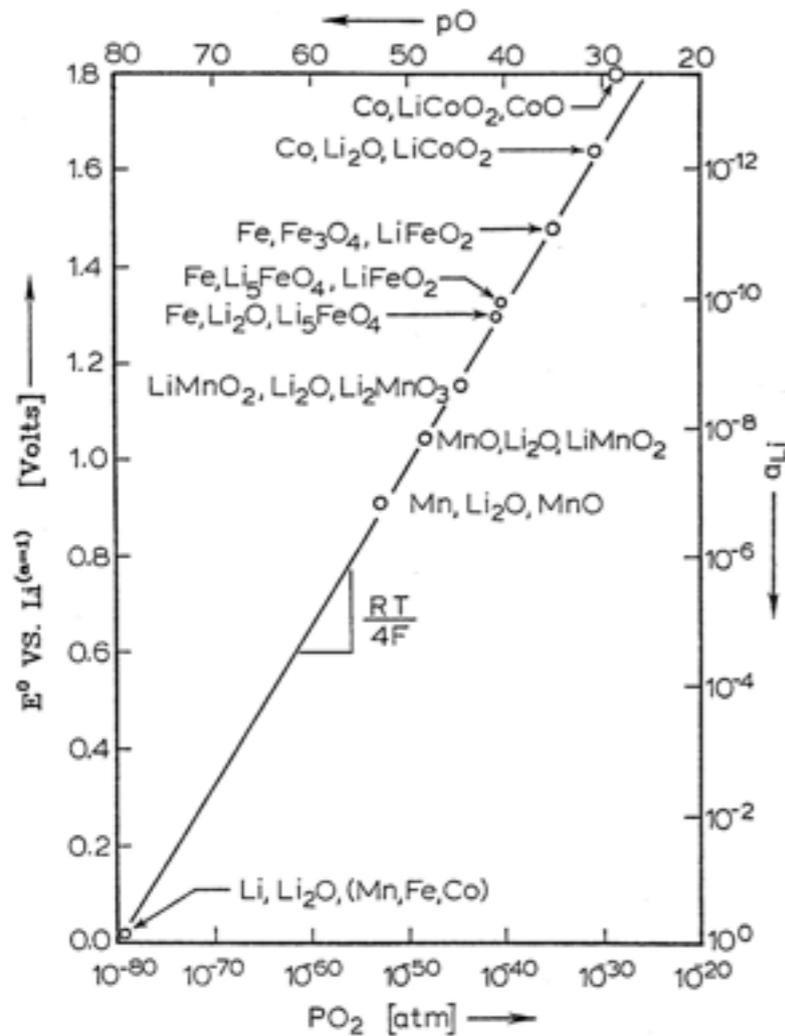
The critical safety issue

Oxide Positive Electrodes in Lithium Systems
Can Have High Equilibrium Oxygen Pressures

Experimental data at Stanford showed a direct
relation between the voltage and the oxygen
pressure.

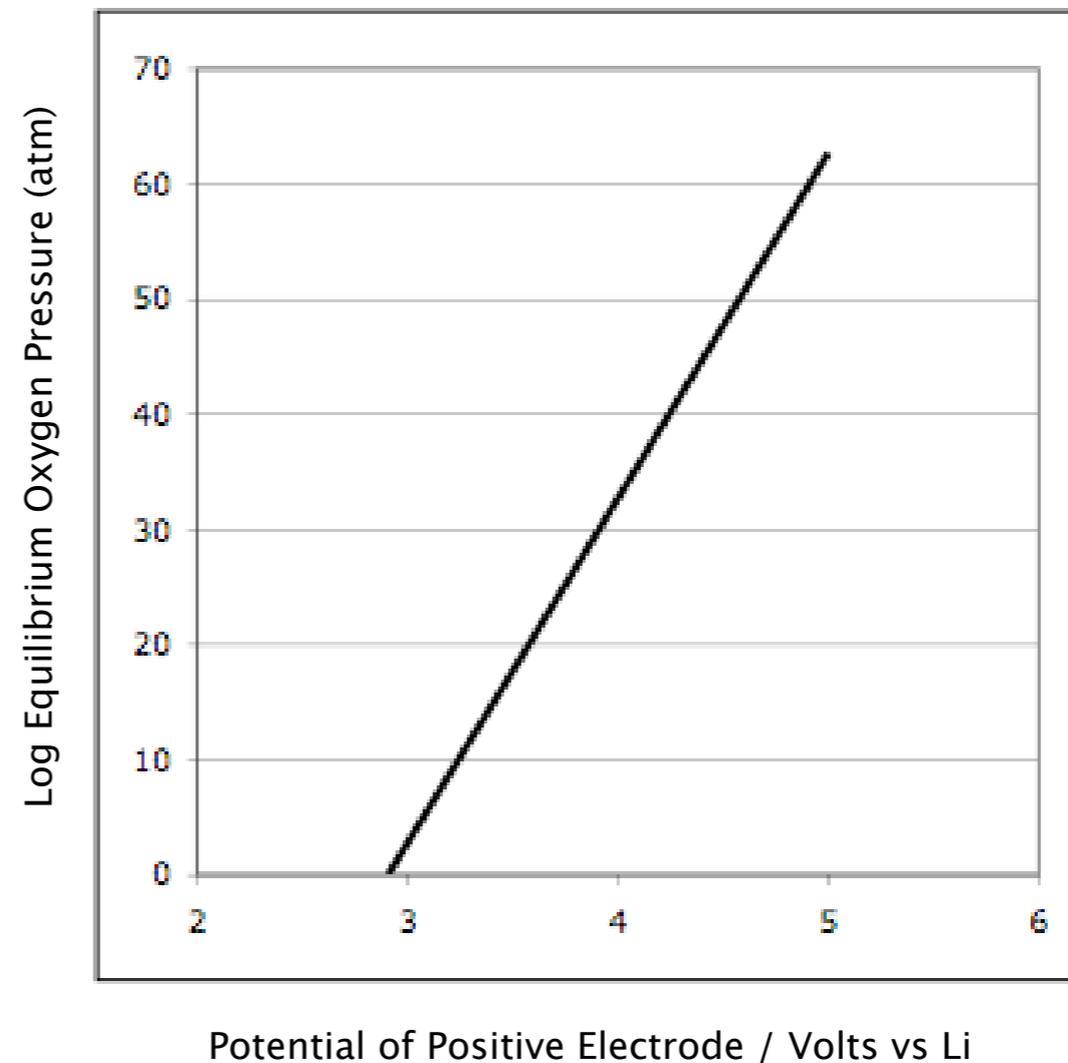
The trend toward higher voltage lithium cells to
store more energy makes this a serious
potential problem.

Early experimental data



Godshall, Raistrick, Huggins, 1984

Extrapolation to higher voltages



At 4 volts, the equilibrium internal pressure becomes very high

Other applications of energy storage are gradually getting more attention

An important one is energy storage to be used to help couple intermittent sources, such as wind and solar, to the electrical grid

In that case, a different set of properties become important from mobile applications

Size and weight are not so critical

Instead, cycle life, calendar lifetime, energy efficiency, safety and cost become paramount

Some of these are interesting new approaches to safe and inexpensive aqueous electrolyte batteries

Major applications are expected to be in non-portable uses, where size and weight are not of prime importance

One is a new approach to inexpensive Pb/acid batteries

The negative Pb,PbSO₄ electrode, the major source of lifetime degradation, can be replaced by finely divided carbon

More interesting is the use of new positive electrodes
and aqueous electrolytes with Na^+ or K^+ ions

Aquion Energy (startup from Carnegie Mellon Univ.)
uses aqueous Na^+ electrolyte
and Na_xMnO_2 positive electrode

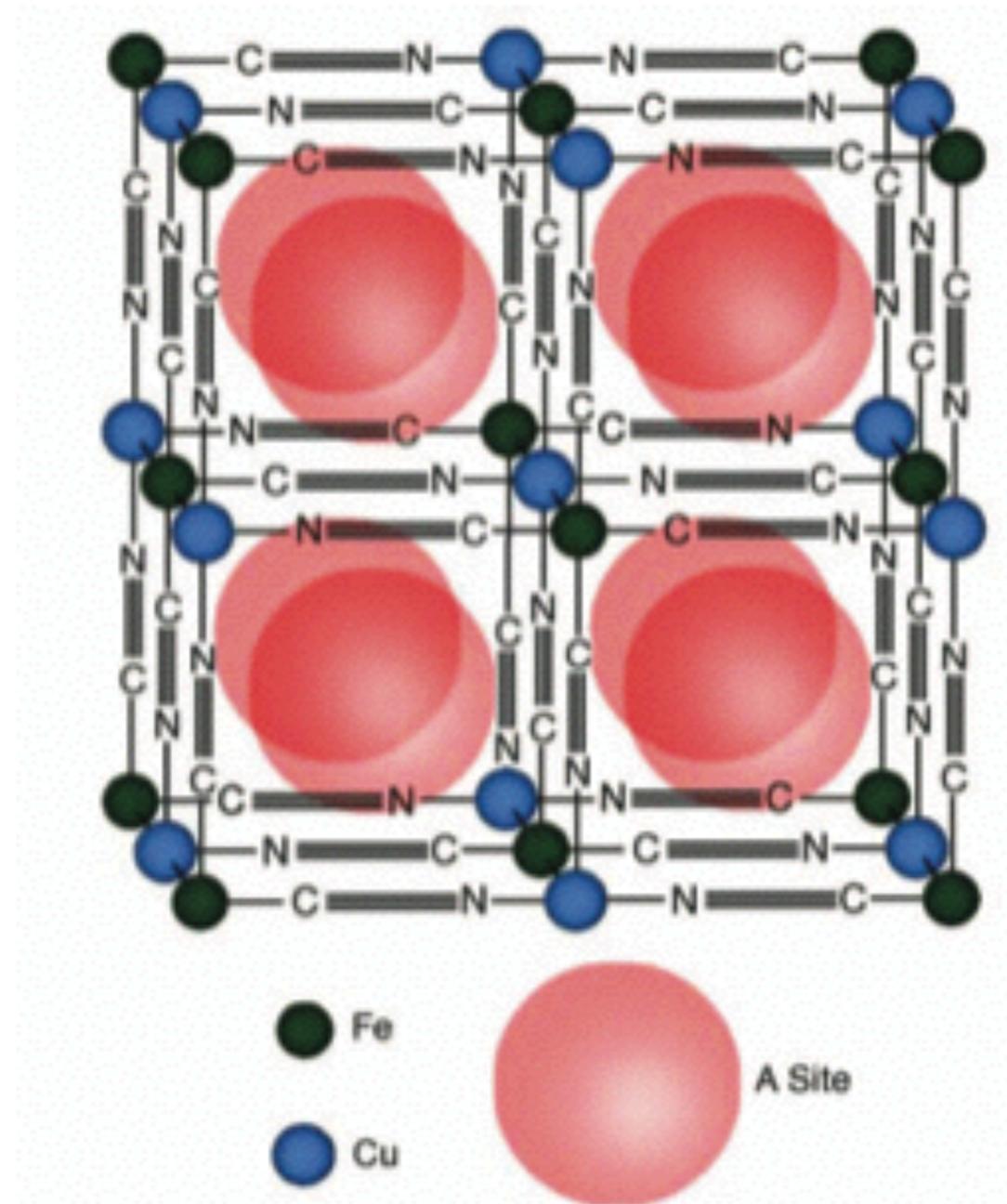
Raised \$50 million in the last year

Now has some 40-50 employees

Currently located in Pennsylvania

Recent Stanford work:

Cells using aqueous Na^+ or K^+ electrolytes and metal-organic open framework positive electrodes



Crystal structure model

Ionic species can go rapidly into and out of the A sites in the open structure

Use of this unusual type of crystal structure results in the possible use of very high rates, with extremely long cycle life

One material in this family has shown no capacity loss after 5,000 fast cycles.

Another had a coulombic efficiency above 99.7 %, and lost only 17% of its initial capacity after 40,000 cycles at a 17 C (complete cycle in 3.5 minutes) rate.

Such new materials are specially interesting for use with rapid, short term transients in wind, solar systems, which no other battery system can handle.

The Great Hopes

There is currently a lot of action chasing two types of battery chemistries that might be very important if they can be made rechargeable.

These are:

The lithium / air system

The lithium / sulfur system

The goal is to get a large amount of energy per unit weight (and cost)

In my view, there are no signs of real success in either case to date

In conclusion:

There is now a lot of research and development effort on improvements and new approaches to batteries.

The range of applications is expanding beyond portable electronics and vehicles, especially in conjunction with new energy sources such as wind and solar.

We are waiting for the next pleasant surprise.

This is the end.

This was a big change in concept

I gave a talk at a conference in Washington in 1972

entitled

“Beta Alumina - Prelude to a Revolution in Solid State Chemistry”

M.S. Whittingham and R.A. Huggins