# Don Lancaster's **Tech Musings**

# July, 1997

n independent researcher has sent me a pair of new energy cells to evaluate. Which he genuinely felt revealed his new battery breakthrough.

The cells easily produced one net watt of power. The electrochemical devices appeared to be solidly based on traditional chemistry and physics. Volume and weight energy densities didn't look that bad either.

The lab work certainly did appear credible and competent.

On the other hand, I felt that the researcher was not nearly as far along as he felt he was. That internal cell resistance appeared way too high to me for any marketable technology. Perhaps by two orders of magnitude or more. His ultimate energy density claims were based upon yet unproven developments. The stability, reaction separation, and longevity seemed not well established. Far more attention did need directed towards studying what others are doing in the field.

Especially on a somewhat similar emerging battery technology.

Unfortunately, not all research is yet on the net. For serious big bucks development on major products, you still have to aggressively seek out the industry insider trade journals or the scholarly pubs. As well as using the tech libraries and conferences.

Be sure to use the premium search services such as *Inspec*, *Compendex*, or *MathSci* found on *Dialog*. All the while realizing that patent searches are at best a minor and a uselessly mind-rotting sideshow. One focusing on losers and failures.

More on doing personal research can be found in PRIMREST.PDF and RESBN60.PDF www.tinaja.com file. More on patents in WHEN2PAT.PDF

These cells did suggest some very interesting column topics...

## **Understanding Source Impedance**

Most any energy supply consists of one or more voltage sources, perhaps with a current source or two, and an unavoidable collection of resistors. A math trick called *Thevenin's Theorem*  tells us that we can always reduce the source to an *equivalent* single voltage in series with a single resistor.

Per figure one.

Thevenin's theorm is very handy to simplify circuit analysis. Should ac sources get involved, there's also likely to be capacitors and inductors present. In which case, Thevenin tells us we can use a single voltage source with a series RLC impedance.

Ferinstance, in a real capacitor, the Thevenin resistance equals the ESR, short for *Effective Series Resistance*. The ESR gets very important in caps used in switch mode power supplies. At higher currents, this ESR causes internal heating and limits rates of charge and discharge. Besides totally trashing efficiency.

All those highly touted supercaps from a decade back never made it out of the gate because their ESR was often ridiculously high for most apps. Some new supercaps based on carbon

Energy density of gasoline Digital temperature sensors Measuring source resistance Online Ulrich's replacement Some electrochemistry basics

> aerogels seem to be solving the high internal resistance problem. *Polystor* is one source. Even using dozens of Farads of supercaps, you'll still have trival total energy storage compared to, say, an AA cell. And absurdly bad voltage regulation to boot.

> In a battery, the Thevenin resistor is called the *internal resistance*. The internal resistance causes heating on charge and discharge. And a possible explosion on a dead short.

> The internal resistance determines your charge-discharge efficiency. It also limits the maximum deliverable current. Internal resistance is usually nonlinear, changing somewhat with load current, moderately with time, and dramatically with state of charge or remaining cell life.

> Just how do you measure a cell's internal resistance? The usual stunt to measure source impedance on plain old electronics is to hang a variable load resistor on your source. Adjust



Fig. 1 – ALMOST ANY ENERGY SOURCE can be replaced for analysis with its Thevenin equivalent of a single voltage source in series with a single internal resistance or impedance. Here is the "two resistor method" I often use to find the equivalent Thevenin values.



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this load until your terminal voltage drops to *one half* of its open circuit value. At this point this load resistor matches your internal one, and your Thevenin source voltage ought to be exactly *double* the output voltage.

This obvious "load to half voltage" route may not perform so great with batteries. Because extreme currents might be involved.

Instead, you can try my alternate method of figure one. You connect a "reasonable" load resistor and then measure its terminal voltage. You'll then *double* the load by placing an identical resistor in parallel. Then you remeasure your terminal voltage. From the *ratio* of these two voltages and the math in figure one, you can calculate a realistic value of internal cell resistance.

An accurate digital voltmeter will be needed any time the cell internal resistance is very low.

Do make sure, of course, that your resistors can handle the power.

A cell's internal resistance consists of two components: Your true value caused by the Ohmic conductance of the electrolyte. Minus a time varying offsetting value of a back-emf from chemical cell depolarization.

Measuring the higher frequency ac impedance of a cell gets ugly in a big hurry. Highly specialized and quite costly instruments are required. The process is called *EIS*. Which is an acronym that means *Electrochemical Impedance Spectroscopy*. *Gamry* is a product and info source.

An aside: There is also the *Norton* equivalent where you replace all the stuff in the box with a single current source and a single internal loading resistor to ground. This is an example of *duality* and can give you another powerful analysis tool. Details in any old circuit theory book.

But note that neither Thevenin or Norton can tell you what is actually going on *inside* of the source. They simply could not care less. A supply having real current sources and real internal resistors to ground will run much hotter and be ridiculously less efficient than a box with real voltage sources and series resistors only.

Voltage sources are most efficient when *open* circuited. Current sources work best when *short* circuited.

#### **Electrochemistry fundamentals**

*Electrochemistry* is that branch of science that handles the conversions of chemical and electrical energy. Your usual electrochemistry starting point is a chapter in any college level *Physical Chemistry* textbook.

Important uses of electrochemistry include batteries, fuel cells, hydrogen production, photosynthesis, corrosion prevention, metal refining, catalysts, electroplating, electroforming, water purification, and electrolysis.

The electrochemistry key is *redox*, or *reduction and oxidation*. Certain chemical reactions *remove* electrons in an *oxidation* process. An oxidation normally takes place at the *anode*, or *most negative* terminal of a *cell*.

Other reactions *add* electrons in a process called *reduction*. Reduction normally will happen at the *cathode*, or *most positive* terminal.

These are typically called *half cell reactions* and *must* be paired.

Many reactions can be *reversible*. Adding external electrons may cause them to proceed in one direction. But forcibly removing electrons causes them to go in the other.

One classic electrochemical cell is shown in figure two. This is called a *zinc-copper galvanic cell*. Multiple cells in series formed a popular early *battery*. We observe an *external* or *conductive* current path through an electric circuit. We have an *internal* or *ionic* current path that can travel through an *electrolyte*.

An electrolyte is any solution in which *ions*, or charged atom(s) which have too few or too many electrons, can freely pass. The conduction of an electrolyte depends upon how many ions are present.

Most electrolytes are liquids.

We basically have got a bucket of glop. Two glops, actually. For there is a porous *separator* in the middle of the cell. This might be some unfired ceramic or anything else that freely could pass ions while preventing the two solutions from mixing.

Other approaches to separation are actual distance, special geometries, or by selective current densities. But you *always* have to keep your anode reaction at the anode and the cathode reaction at the cathode.

Otherwise, your cell shorts out.

The glop starts out as a sulphuric acid and water solution. But zinc in acid readily becomes an ionic zinc sulphate solution on the left. Copper in acid readily forms an ionic copper sulphate solution on the right.

Your left glop is a zinc electrode anode in a zinc sulfate solution. The right glop will be a copper cathode in a copper sulphate solution.

Not all elements are equally likely to ionize. Thus, the favored zinc goes into solution, giving up electrons to the anode in its oxidation reaction. The zinc anode gets *smaller* as more and more of it reacts into the ionic zinc sulphate solution.

The electrons go out through your external electric circuit and return to your copper cathode. These electrons should combine with the copper ions and reduce elemental copper out onto the cathode. The copper cathode thus gets *larger* as more and more ions are converted by the incoming electrons.

Meanwhile, negative sulphate ions are traveling from left to right, thus driving the external electron flow.

As more and more electical energy is removed, the remaining chemical energy will deplete. Conservation of energy and all. When all of the zinc is gone, the process stops.

This process is reversible. If you apply external electric energy from a *current source* (such as any current limited generator or another battery), you can force the electrons to go in the other direction. In which case, the copper goes into ionic solution and thus releases electrons.

While the zinc goes out of solution by consuming electrons. This time around, the zinc is getting bigger and the copper smaller.

How does that big ole minus sign end up on an *anode*? In any vacuum tube, the electrons all go from the cathode to the anode.

In a discharging electrochemical cell, the negative ions also all travel from the cathode to the anode. But since the anode is the electron *source* 

ELECTRODE ELEMENT	POTENTIAL REACTION	SERIES VOLTAGE
Lithium	$Li \leftrightarrow Li^+$	-3.00
Rubidium	$Rb \leftrightarrow Rb^+$	-2.93
Potassium	$K \leftrightarrow K^+$	-2.92
Barium	Ba ↔ Ba <sup>++</sup>	-2.90
Strontium	$Sr \leftrightarrow Sr^{++}$	-2.90
Calcium	$Ca \leftrightarrow Ca^{++}$	-2.87
Sodium	$Na \leftrightarrow Na^+$	-2.72
Magnesium	$Mg \leftrightarrow Mg^{++}$	-2.37
Aluminium	$AI \leftrightarrow AI^{+++}$	-1.67
Manganese	$Mn \leftrightarrow Mn^{++}$	-1.10
Zinc	$Zn \leftrightarrow Zn^{++}$	-0.76
Chrominium	$Cr \leftrightarrow Cr^{+++}$	-0.70
Iron	$Fe \leftrightarrow Fe^{++}$	-0.44
Cadmium	$Cd \leftrightarrow Cd^{++}$	-0.40
Indium	$ln \leftrightarrow ln^{+++}$	-0.34
Thallium	$TI \leftrightarrow TI^+$	-0.34
Cobalt	$Co \leftrightarrow Co^{++}$	-0.28
Nickel	$Ni \leftrightarrow Ni^{++}$	-0.25
Tin	$Sn \leftrightarrow Sn^{++}$	-0.14
Lead	$Pb \leftrightarrow Pb^{++}$	-0.13
Hvdrogen	$Pt/H_{a} \leftrightarrow H^{+}$	0.00
Antimony	$Sb \leftrightarrow Sb^{+++}$	+0.15
Bismuth	$Bi \leftrightarrow Bi^{+++}$	+0.20
Arsenic	$As \leftrightarrow As^{+++}$	+0.30
Copper	$Cu \leftrightarrow Cu^{++}$	+0.34
Oxvaen	$Pt/OH^- \leftrightarrow O_2$	+0.40
Silver	$Aa \leftrightarrow Aa^+$	+0.80
Mercury	$Hq \leftrightarrow Hq_{2}^{++}$	+0.80
Palladium	$Pd \leftrightarrow Pd^{++}$	+0.83
Gold	$Au \leftrightarrow Au^+$	+1.70

Fig. 3 – ELECTRODE POTENTIAL SERIES determines the output voltage of an electrochemical cell. Output voltage is the difference of the anode and cathode potentials. On a zinc-copper cell, 0.34 - (-0.76) = 1.10 volts.

for the rest of your electrical circuit, the cell's anode ends up as the most *negative* terminal in your system.

While discharging, your electron flow in figure one is *clockwise*, while your standard conventional current is *counterclockwise*. Do note that your arrow on the charging current source points in the *conventional current* (or *hole* travel) direction.

The electrons go the other way.

Where does the cell voltage come from? Once again, zinc has a greater tendency to ionize than does copper. These tendencies form what is known as the *electrode potential series* (or *electromotive series*) of figure three. And are usually compared against a neutral or *hydrogen electrode*. We see that zinc has a tendency to reduce that is -0.76 volts less than neutral. Copper really does like to reduce, so its reduction ionization tendency is positive by 0.34 volts. Together these subtract to 1.10 volts. Which is the theoretical open circuit voltage of a zinc-copper cell.

Terminal electrode potentials are related to the oxidation potentials and reduction potentials of the involved reactants. See any physical chemistry book for all the gory details.

You can make an electrochemical cell by placing a nail and a copper wire into a lemon.

A lot of electrochemistry was done over a century ago, so there is a rich body of literature to tap. Chances are your "new" idea has been thoroughly plowed. On the other hand, there are some really big bucks waiting for the first practical solar cell replacement that mimics photosynthesis. Or for improved laptop computer or cellular



# **Tech Musings**

Advanced Battery Tech	Catalysis Reviews	Electrodeposition	Jnl of Solution Chem
913 Trssler Street	270 Madison Avenue	2540 Olentangy River Road	233 Spring Street
Boalsburg PA 16827	New York NY 10016	Columbus OH 43210	New York NY 10013
(814) 466-6559	(800) 228-1160	(800) 848-6538	(212) 620-8000
Analytical Electrochem	<b>Chemical Abstracts Svc</b>	<b>EPRI Journal</b>	Metal Finishing
2540 Olentangy River Road	PO Box 3012	PO Box 10412	126 Oakley Avenue
Columbus Oh 43210	Columbus OH 43210	Palo Alto CA 94303	White Plains NY 10601
(800) 848-6538	(800) 848-6538	(415) 855-2000	(914) 333-2500
Assn Battery Recyclers	Doklady Physical Chemistry	Gamry Instruments Inc	Plating & Surface Fin
PO Box 707	233 Spring Street 5th Fl	607-C1 Easton Road	12644 Research Pkwy
Troy AL 36081	New York NY 10013	Willow Grove PA 19090	Orlando FL 32826
(334) 566-1563	(212) 620-8000	(215) 830-9886	(407) 281-6441
Battery & EV Technology	<b>Electroanalysis</b>	Home Power	Rocky Mountain Inst
25 Van Zant Street #13	303 NW 12th Avenue	PO Box 520	1739 Snowmass Creek R
Norwalk CT 06855	Deerfield Beach FL 33442	Ashland OR 97520	Snowmass CO 81654
(203) 853-4266	(954) 428-5566	(916) 475-3179	(970) 927-3851
Battery Council Intl	Electrochemical Society	Intl Jnl Hydrogen Energy	Russian Jnl Electrocher
401 N Michigan Avenue	10 S Main Street	The Boulevard, Langford Lane	233 Spring Street
Chicago IL 60611	Pennington NJ 08534	Kidlington, Oxford OX5 1GB	New York NY 10013
(312) 321-6610	(609) 737-1902	UK	(212) 620-8000
Battery Man, The	Electrochem Technology	<b>Jnl Electroanalytical Chem</b>	Solid State Ionics
100 Larchwood Drive	10 South Main Street	Box 882 Madison Sq Sta	PO Box 211
Largo FL 34640	Pennington NJ 08534	New York NY	1000 AE Amsterdam
(813) 586-1408	(609) 737-1902	(212) 989-5800	The Netherlands
Biosensors & Bioelect	Electrochimica Acta	Jnl of Power Sources	Surface Engineering
The Boulevard, Langford Lane	655 Avenue of Americas	PO Box 564	150 5th Avenue #1001
Kidlington, Oxford OX5 1GB	New York NY 10010	1001 Lusanne	New York NY 10024
United Kingdom	(212) 633-3903	Switzerland	(212) 924-3950

Do note that there are all sorts of hazardous materials involved with all electrochemical lab work. Everything from cyanide to hydrogen.

A good set of electrochemical web links is at www.electrochem.org/ecs/ intpgs.html Also check www.cmt.anl. gov/estir/info.html Plus the book list at .../books.htm The Amazon Books folks at www.amazon.com list 600+ electrochemistry books.

The Usenet newsgroups do include *sci.chem.electrochem* along with that *sci.chem.electrochem.battery* I have arranged a few other places to go for useful help on electrochemistry in this month's resource sidebar.

## **Energy Density of Gasoline**

The "cubic goodness" of any new battery technology gets measured by its *energy density*. Using a pair of numbers. One tells you the weight of the cell for the punch delivered. And is usually measured in *watt hours per kilogram*. The second tells you how much room the cell takes up for the For instance, lead acid often uses energy densities of 25 watt hours per kilogram and 60 watt hours per liter. Lithium can provide 400 wh/kg and up to 1000 wh/l.

The ratio of your volume density to the weight density always seems to stay roughly between two and three. From light lithium up to heavy lead. And for everybody else. Regardless of the battery technology. As long as electrochemistry is used.

## NEED HELP?

Phone or write all your US Tech Musings questions to:

> Don Lancaster Synergetics Box 809-EN Thatcher, AZ, 85552 (520) 428-4073

US email: *don@tinaja.com* Web page: *www.tinaja.com*  The obvious question for electric cars is "How does the battery energy density compare to gasoline?" Yeah, you have got an apples-to-oranges situation, but I've been unable to find any published source for the energy density of gasoline. A free *Incredible Secret Money Machine II* if you can lead me to one.

Instead, let's fish out the good old *Handbook of Chemistry and Physics* from *CRC Publishing*. Which tells us that gasoline can deliver just under 21,000 BTU's per pound. And from a MSDS sheet, we find that the specific gravity of gasoline is 0.71.

A kilogram is 2.2 pounds, so we get 46,200 BTU's per kilogram. Since a liter of water weighs one kilogram, we get around 32,802 BTU's per liter when we adjust for gasoline's lower specific gravity.

Now, a kilowatt hour equals 3413 BTU's, so we will get 13.54 kilowatt hours per kilogram. Equal to 13,540 watt hours per kilogram.

And, again adjusting for specific gravity, about 9613 wh/l.



## NAMES AND NUMBERS

Analog Devices PO Box 9106 Norwood MA 02062 (617) 329-4700

Applied Microwave & Wireless 2245 Dillard Street Tucker GA 30084 (770) 908-2320

California Eastern Labs 4590 Patrick Henry Dr Santa Clara CA 95054 (408) 988-3500

**Clement Engineering** PO Box 1086 Severna Park MD 21146 (410) 268-6736

Dallas Semiconductor 4401 Beltwood Pkwy S Dallas TX 75244 (214) 450-0400

Dialog Info Svcs 3460 Hillview Ave Palo Alto CA 94304 (415) 858-2700

In Vivo Metric PO Box 249 Healdsburg CA 95448 (707) 433-4819

Intele-Card News PO Box 9739 The Woodlands TX 77387 (713) 362-7141 Last Straw PO Box 42000 Tucson AZ 85733 (520) 882-3848

MedianiX 100 View Street Ste 101 Mountain View CA 94041 (415) 960-7081

National Semicon 2900 Semiconductor Rd Santa Clara CA 95052 (800) 272-9959

Navtech Info Svc 2775 S Quincy St #610 Arlington VA 22206 (800) NAV-0885

**Oxbridge** 150 5th Ave #202 New York NY 10011 (212) 741-0231

Plessey/GEC 1500 Greenhill Rd Scotts Valley CA 95067 (408) 438 2900

**Synergetics** Box 809 Thatcher AZ 85552 (520) 428-4073

Unlimited Fun Options Box 119A Kingston NM 88042 (505) 895-5608

On a weight basis, gasoline is thus 542 times better than lead acid, and 34 times better than lithium. And on a volume basis, gasoline is 160 times better than lead acid and around 9.6 times better than lithium.

Uh, that suggests that a 20 gallon tank of gasoline weighing 116 pounds might get replaced by a mere 69,736 pounds of lead acid batteries.

Yeah, you will have to adjust for delivered efficiencies and such. But no matter how much you fudge those numbers, we clearly ain't there yet with today's battery technology.

Not by a country mile.

It is difficult not to conclude that hybrid vehicles make an awful lot of sense, while the pure electrics remain monumentally stupid.

Lots more on hybrid vehicles from Amory Lovins at his *Rocky Mountain Institute*. At *www.rmi.org* As well as in *Home Power* magazine.

Two good battery texts include the Handbook of Batteries & Fuel Cells from *McGraw Hill* and that *Battery Reference Book* sold by *Butterworth Heinemann*. Additional resources on batteries appears in RESBN58.PDF on my *www.tinaja.com*.

#### Ulrich's move over

I have long been a fan of *Ulrich's Periodicals Dictionary*. Back in hard copy, this has been by far your most important technical tool. Anytime ever. Ulrich's tells you about all the trade journals, user magazines, and scholarly pubs available everywhere in the world. Around 85,000 of them. Needless to say, these trade journals are essential for electronics.

But I have yet to find Ulrich's on the web. I strongly feel their "must subscribe" policy on their CD ROM's is outrageously snotty.

Numero dos in hard copy was the International Standard Periodicals Dictionary from Oxbridge. But these people are now freely online at their www.mediafinder.com And you can

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# **Tech Musings**



Fig. 4 – ANALOG DEVICES TMP03/04 temp sensor has a digital output.

instantly search on keywords. They are now ridiculously cheaper, faster, and better than Ulrich's.

While useful and handy, I did find some minor problems. Such industry trader journals as *ITS World* or *EDM Today* are not yet listed. But because you can instantly list yourself online, I would expect most mags to shortly appear. Their direct contact service also does not seem to work. Out of two dozen media kit requests, I have yet to receive a single one.

Speaking of which, let's repeat the usual scam: The way to get a review copy of most any ad-supported mag is to contact their ad department and request a *media kit*. This sometimes gets you a free subscription as well. I call this the *SCAR* technique, short for *sample copy & ad rates*.

More on all this in my *Incredible* Secret Money Machine II and in my Resource Bin reprints.

#### **Integrated Thermometers**

Semiconductor sensors have now gone way beyond simple temperature measurement. They now include such features as built in set points, a full thermostatic action, deadbands, and elaborate digital comm.

Sometimes over a single wire.

Two leading sources here include *Dallas* and *Analog Devices*.

I've been meaning to do a roundup on these, but let's instead look at two examples. Figure four shows us the *Analog Devices* TMP03 and TMP04 sensors. Which can directly measure temperature and output it as a digital data stream to a microcontroller.

Their temp output is a duty cycle modulated waveform from 20 to 50 Hertz. Your high time is fixed at 10 milliseconds. The low output time is proportional to the temperature. A fairly simple duty cycle calculation as shown gives you the temperature in Farenheit or Centigrade.

The operating range is -40 to +100 degrees centigrade. Typical accuracy is half a degree. Response time varies with the package, being 25 seconds in free air for their T0-92 "transistor" pack and 50 seconds for the eight pin SO-8 minidip. Operating current is just under one mil at five volts.

The -03 is open collector, while the -04 gives a TTL/CMOS compatible output. Either interfaces beautifully with the *Basic Stamp* from *Parallax*  or any old PIC. More details on these are found on the PIC Library Shelf of my *www.tinaja.com* 

## New Tech Lit

On the GPS front, the new *Global Positioning Products Handbook* from *Plessey*, a single chip GPS receiver front end by *California Eastern Labs*, and scads of products and info from *Navtech GPS Supply*.

From *National Semiconductor* a free *Transmission Line Rapidesigner* slide chart. From the *MedianiX* folks, data sheets on the unique MED25101 Digital Karaoke Audio Processor and a MED25005 Surround Sound Chip.

Clement Engineering has a low cost telemetry circuit for use with balloons and such. Biopotential skin electrodes get sold by *In Vivo Metric*.

New trade journals for this month include Intele-Card News on phone cards Along with Applied Microwave & Wireless on high frequency comm.

The Last Straw is a newsletter on straw bale home construction. Check out their Role in the hay classifieds.

The newest of Levitrons now levit higher. Up to *twenty four* hours and longer! Contact Mike Sherlock at his *Unlimited Fun Options* for details.

To pick up all the fundamentals of digital integrated circuits, check my *TTL Cookbook* and *CMOS Cookbook*. The latter is now freshly republished by *Butterworth Heinemann*. It should now be stock in all major bookstores. Autographed copies are available per my nearby *Synergetics* ad.

I've just added an "automatic news group finder" as a NEWSLIST.HTML on my *www.tinaja.com* You also can find bunches of reprints here, surplus bargains, a consultant's network, and annotated hot links to lots of unusual and useful web locations.

Most of the mentioned items do appear in the *Names & Numbers* or *Electrochemical Resources* sidebars. Be certain to check here first before calling our US tech helpline.  $\blacklozenge$