ENVIRONMENTAL VEHICLES '94

...National Challenges for the Commercialization of Clean Fuel Vehicles...

CONFERENCE PROCEEDINGS

Sponsored by:

25-26 January 1994

Dearborn Inn
Dearborn, Michigan

THEORETICAL LIMITS TO APPLICATION OF BATTERIES FOR AUTOMOBILE PROPULSION
(SYSTEM STUDY)

Alex J. Severinsky, Ph. D.
General Partner
PAICE R&D, L.P.

ABSTRACT

A theoretical electrochemical cell is designed for the highest practical energy density. All materials are selected on the basis of bonding energies of the elements in the periodic table. It is shown that physical limit to energy density of batteries is 13 times larger than in lead-acid batteries and an optimistic practical limit is approximately 450 Wh/kg. Engineering estimates are made for required weight and optimistic cost of such imaginary batteries in the existing off-the-shelf passenger automobiles. Comparison is made between economics of gasoline, ethanol, and such imaginary batteries as sources of energy for automobile propulsion.

INTRODUCTION

In the past 100 years there were numerous attempts to develop electric cars with rechargeable batteries as an alternative automotive system. Despite considerable investment, all attempts have failed.

This paper presents theoretical limits on energy density in practical batteries, describes several theoretically possible the most energy dense batteries in a new combination of materials, and compares them with conventional energy sources for automotive propulsion.

The content is presented in the following order: battery definition, physics of the electro-chemical processes, analysis of materials, cell type analysis, analysis of a system of the automobile and the battery, and comparison of economics of alternate energy sources.

DEFINITION OF A BATTERY

The battery is defined from historical retrospective in relation to its application in automobiles as a practical energy source.

Construction wise, the battery consists of several electro-chemical cells connected in series. A cell contains, as a minimum, two metal electrodes to conduct electric current and an electrolyte between them.

Every cell is capable of storing and releasing electric energy passing through electrodes by means of chemical change of electrodes and/or an electrolyte. The energy efficiency of store and release cycle is close to 100%.

The battery is capable of operating without degradation in performance in full automotive temperature range -40oC to + 85oC. Neither heating or cooling of it is required.

The battery materials are not irreversibly consumed during its operation from any practical viewpoint.

Poisonous, explosive, technologically expensive, or rare earth materials are not utilized.

This definition of the battery will be used during the search for its most energy dense combination of materials, processes, and structures.


PHYSICS OF ELECTRO-CHEMICAL PROCESSES

The main phenomena which determines energy transformations in electro-chemical processes is the difference in electron bonding energy (work function) in two different conductors of electric current, usually metals. We will start analysis from metals and later on will show that other electric current conductors - electrolytes - lead to lower energy density.

When we bring metals in contact, there appears the voltage potential across the contact due to the difference in electron bonding energy. When we complete the electric circuit to measure the potential, we bring other ends of metals in contact. Then, another potential of the same magnitude, but opposite polarity, develops totally canceling the first one. To weaken the cancellation, several different ways could be chosen. One is to change the temperature of one junction which in its turn
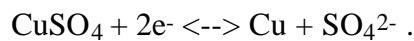
changes the difference in electron bonding energy in metals. It is especially vivid in semiconductors. This is a well-known thermo-electric effect.

Another possibility is to separate metals at one junction and change electron bonding energy at both ends unequally, by bonding metal atoms differently, in other words, put metals in chemical reactions. The media surrounding metals shall be a source of those reactions, moreover, it shall be a conductive source to complete the electric circuit and realize the voltage potential difference - electrolyte. This is galvanic effect.

The vivid demonstration of this effect is in Daniel's element. Zn and Cu are used as electrode metals. Both electrodes are immersed in $ZnSO_4$ and $CuSO_4$ electrolytes correspondingly. The electrolytes are separated with the membrane permeable for SO_4^{-2} ions. On Zn electrode, the reaction is:

$$Zn + SO_4^{-2} \quad <--> ZnSO_4 + 2e^-;$$

and on Cu Electrode:

$$CuSO_4 + 2e^- <--> Cu + SO_4^{2-} .$$
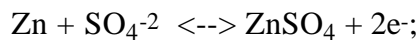
The voltage potential of the cell is determined by the difference in the electron bonding energy or electrically equivalent ionic bonding energy of Zn ions in the metal and in Zinc sulfate electrolyte and Cu ions in Copper sulfate electrolyte and in the metal. The process on Zn electrode is called oxidation, release of electrons, and on Cu electrode - reduction, intake of electrons. The whole process is most commonly called electrochemical process, the reaction - oxidation/reduction reaction, and the structure - electrochemical cell.

The voltage potentials of oxidation/reduction of elements, ions, and various compounds in comparison with a standard Hydrogen electrode is well tabulated. The potential of this Hydrogen electrode is arbitrarily set at zero. Let's designate these voltage potentials versus Hydrogen electrode as Vm.

One can easily calculate the voltage potential of a cell (Vc) based on the knowledge of oxidation/reduction reactions taking place during charge or discharge as an algebraic sum of such individual voltage potentials.

$$V_c = V_{m1} + V_{m2} + ... = \Sigma V_{mi} .$$

Faraday's law allows to calculate the energy density of a cell reaction - E. The law states that 96,500 Coulombs (F) of electric charge will be released by one gram-equivalent weight of matter. The gram-equivalent weight is molecular weight of all elements of the reaction expressed in grams (M) divided by the number of electrons (n) released/consumed by the reaction:

$$M_e = M/n.$$

Combining the equations for cell voltages and Faraday's law, we receive the following

formula for energy density:

$$E = (\sum V_{mi})*F/(M/n), \text{ in Watt-sec/gram.} \qquad \text{Eq.1}$$

The above formula for energy density can be applied under ideal condition of a) complete conversion of chemical bonding energy into electrical energy and b) infinitely diluted electrolytes. Below, we will define corrections for this formula to reflect the actual and not ideal conditions.

Another energy process necessarily taking place in the cell is mutually complimentary chemical change of electrode materials or change in electrolyte composition. In our example, the sulfate ion SO_4^{2-} initially was ionicly bonded to Cu^{2+} ions in one solution but finally to Zn^{2+} ions in another solution. The change in bonding energy of the negative ion is small only if diluted solutions are utilized and when positive ion sizes are close to each other. In cases where the metal compounds are lightly soluble and form layers on electrodes, like in rechargeable cells, and when metal atoms bond radii are of considerable difference, that energy difference could be significant. It even can be the major force in the cell as in cells with liquid junctions. The value of that energy change can be estimated by comparing the length of chemical bonds or crystal ionic radii, or strength of chemical bonds and crystal structures, or heats of formations (enthalpies - H) and associated changes in entropy. The change in entropy deserves our special attention. If there is a difference in entropy of initial and final products of electrochemical reaction, the available free energy released in the electric circuit will differ from the change in enthalpy by that amount. The difference can be both positive and negative. Gibbs-Helmholtz equation takes this phenomena in consideration in the following formula:

$$\Delta H/F*n = \sum V_{mi} - T*(d(\sum V_{mi})/dT). \qquad \text{Eq.2}$$
$$\text{where } \Delta H \text{ - change in enthalpy, and } T \text{ - absolute temperature.}$$

Theoretical energy efficiency of the cell can be found by correction on the change in entropy or by using Eq.2 when the temperature coefficient of the cell voltage is known. The magnitude of correction can be significant only if initial and final products of the reaction are in different states like solid, liquid, or gaseous. When that is not the case, the difference in entropy is negligible for all practical purposes, the temperature coefficient is close to zero, and the cell thermodynamic efficiency is close to 100%.

The ionic bonding energy of metal compounds in the solution depends on density of other ions or on concentration.
The relation between the cell voltage and concentration of ions in electrolyte was found by Nernst:

$$V = V_o - (R*T/n*F)\ln Q, \qquad \text{Eq.3}$$

where: V - actual cell potential; V_o - potential at infinite dilution; R - gaseous constant; T - absolute

temperature; n - number of transported electrons; F - Faraday constant; Q - value, associated directly with ion concentration.

For a generalized cell reaction:

$$wA + xB \longleftrightarrow yC + zD; \hspace{4cm} \text{Eq.4}$$

where A, B, C, D - are concentrations of reactants participating in the reaction in quantities w, x, y, z.

$$\text{Then } Q = (C^yD^z)/(A^wB^x). \hspace{4cm} \text{Eq.5}$$

In practice, the concentration influence is usually very small as the value $R*T/F*\log(e)$ is approximately 0.06 V.

ANALYSIS OF MATERIALS

The analysis of materials is based on physics of the cell and is directed toward achievement of maximum energy density, the main characteristic of the battery for automotive propulsion.

The most important materials in the cell are electrode metals. The analysis begins from the elementary metals. Then we will consider intermetallic compounds while trying to improve the results. The starting point is the analysis of energy density of metal oxidation-reduction reactions in relation to the metal ion itself. The results of the analysis are summarized in Table 1.

TABLE 1
METAL ENERGY DENSITIES

Atomic Number	Reaction						Vm	M	Emr
3	Li^+	+	e^-	↔	Li		-3.04	7	0.43
4	Be^{2+}	+	$2e^-$	↔	Be		-1.70	9	0.38
11	Na^+	+	e^-	↔	Na		-2.71	23	0.12
12	Mg^{2+}	+	$2e^-$	↔	Mg		-2.38	24	0.20
13	Al^{3+}	+	$3e^-$	↔	Al		-1.66	27	0.18
19	K^+	+	e^-	↔	K		-2.92	39	0.075
20	Ca^{2+}	+	$2e^-$	↔	Ca		-2.76	40	0.14
21	Sc^{3+}	+	$3e^-$	↔	Sc		-2.08	45	0.14
22	Ti^{3+}	+	$3e^-$	↔	Ti		-1.75	48	0.11
23	V^{2+}	+	$2e^-$	↔	V		-1.20	51	0.048
24	Cr^{6+}	+	$6e^-$	↔	Cr		-0.43	52	0.050
25	Mn^{2+}	+	$2e^-$	↔	Mn		-1.03	55	0.038
26	Fe^{2+}	+	$2e^-$	↔	Fe		-0.44	56	0.016
27	Co^{3+}	+	$3e^-$	↔	Co		+0.43	59	0.021
28	Ni^{2+}	+	$2e^-$	↔	Ni		-0.25	59	0.085
29	Cu^{2+}	+	$2e^-$	↔	Cu		+0.34	64	0.011
30	Zn^{2+}	+	$2e^-$	↔	Zn		-0.76	65	0.0058
31	Ga^{3+}	+	$3e^-$	↔	Ga		-0.56	70	0.024
46	Pd^{2+}	+	$2e^-$	↔	Pd		+0.83	106	0.016
47	Ag^+	+	e^-	↔	Ag		+0.80	108	0.0074
78	Pt^{2+}	+	$2e^-$	↔	Pt		+1.2	195	0.012
79	Au^{3+}	+	$3e^-$	↔	Au		+1.42	197	0.022
80	Hg^{2+}	+	$2e^-$	↔	Hg		+0.85	201	0.0084

In this table, V_m - metal's reduction potential, M - atomic weight, E_{mr} - relative energy density - $V_m/(M/n)$. There are shown metals with the highest energy density which are the lightest ones, and metals with the largest positive potentials necessary for further analysis. For some reactions, the reduction potential was calculated as a gram-equivalent weighted average of two sequential ion reduction potentials, like from Fe^{3+} to Fe^{2+} following with Fe^{2+} to Fe.

The data shows that energy density rapidly decreases with the increase in atomic weight, especially for the lightest metals. This is the result of a double effect of reduction of electron bonding energy due to a larger ion radius and increase of atomic weight.

The best metals for one of the cell electrodes are in order - Li; Be; Mg; Al; Na. Among them Li; Mg; and Na are highly reactive. It will be almost impossible to protect them from irreversible corrosion in practice. The example of such difficulty is a well-known corrosion problem in sodium-sulfur batteries. Among Be and Al, we have to choose Al because Be is almost hundred times more expensive and, more importantly, extremely toxic. Al is our best choice for one of the cell electrodes from standpoint of a practical battery as initially defined.

Now, let's find out if there is any intermetallic compound which might be better than A1. Analyzing the physical properties of the most energy dense metals, we notice that the voltage potential increases with the decrease of the ion electric charge and atomic size. Most likely, the repelling force between ions in the metal, roughly proportional to (ne)2/r (n - metal ion valence; e -

electron charge; r - metal ion radius), is the cause of increase in the voltage potential. If we are to simulate this phenomena in any intermetallic compound, the best we could do is to bond Al and Be in such a way that they have double covalent bond in between and one bond available for metal ionic bonding. The potential we can hope to achieve, even without counting on large molecular size, is the one of Li. The mass of Al-Be compound is 36, so the expected Emr < 0.083. It is even worse than in any metal of the compound as majority of their energy carrying bonds are not used.

Finally, Aluminum is our best choice for the first electrode.

The selection of the metal for the second electrode is not as autonomous as for the first one. It is dependent on energy density characteristic of Al electrode. Now, it is necessary to match the second metal with Al in such a way that the largest common energy density is achieved. The latter is the weighted average of both metals:

$$E_{m1m2r} = (E_{m1r}M_{1e} + E_{m2r}M_{2e})/(M_{1e} + M_{2e}); \qquad\qquad Eq.6$$

where E_{m1m2r} - relative energy densities of two metals; M1e and M2e - gram-equivalents of metals.

The results of calculation for E_{m1m2r} for the number of the best combinations with Al are shown in Table 2.

TABLE 2
ALUMINUM - METALS ENERGY DENSITIES

Atomic Number	Reaction			Vm	Me	E_{m1m2R}	Priority
23	V^2	$+ \; 2e^- \leftrightarrow$	V	-1.2	25.5	0.013	
24	Cr^{3+}	$+ \; 3e^- \leftrightarrow$	Cr	-0.74	17.3	0.035	
24	Cr^{6+}	$+ \; 6e^- \leftrightarrow$	Cr	-0.43	8.7	0.070	2
25	Mn^{2+}	$+ \; 2e^- \leftrightarrow$	Mn	-1.03	27.5	0.017	
25	Mn^{3+}	$+ \; 3e^- \leftrightarrow$	Mn	-0.18	18.3	0.054	4
26	Fe^{3+}	$+ \; 3e^- \leftrightarrow$	Fe	-0.036	18.7	0.059	3
27	Co^{2+}	$+ \; 2e^- \leftrightarrow$	Co	-0.28	29.5	0.036	
27	Co^{3+}	$+ \; 3e^- \leftrightarrow$	Co	+0.43	19.7	0.073	1
28	Ni^{2+}	$+ \; 2e^- \leftrightarrow$	Ni	-0.25	29.5	0.037	
29	Cu^+	$+ \; e^- \leftrightarrow$	Cu	+0.52	64	0.030	
29	Cu^{2+}	$+ \; 2e^- \leftrightarrow$	Cu	+0.34	32	0.049	5
30	Zn^{3+}	$+ \; 2e^- \leftrightarrow$	Zn	-0.76	32.5	0.022	
31	Ga^{3+}	$+ \; 3e^- \leftrightarrow$	Ga	-0.56	23.3	0.034	
46	Pd^{2+}	$+ \; 2e^- \leftrightarrow$	Pd	+0.83	53	0.040	
47	Ag^+	$+ \; e^- \leftrightarrow$	Ag	+0.80	108	0.021	
78	Pt^{2+}	$+ \; 2e^- \leftrightarrow$	Pt	+1.2	97.5	0.027	
79	Au^{3+}	$+ \; 3e^- \leftrightarrow$	Au	-1.42	65.7	0.041	
80	Hg^{2+}	$+ \; 2e^- \leftrightarrow$	Hg	+0.85	100.6	0.023	

The data show that the best matching metal ions with Al are in order Co^{3+}; Cr^{6+}; Fe^{3+}; Mn^{3+}; and Cu^{2+}. The noble metals, while having large positive potentials and providing in such way the overall large cell potential, are at a disadvantage from energy density view point because they are heavy. So, their use is restricted primarily not by cost but by lower technical characteristics.

Now, it's again time to analyze if we could do better by using some intermetallic compound. The comparison of physical properties of elements aim us at the compound inert at least as gold to have the large positive potential but much lighter than gold to match or outperform Cobalt. Let's imagine that two light transition metals with average atomic mass of 60 each are as inert as gold in intermetallic compound, so the potential is 1.4V and valence is 3. Then E_{m1m2r} will be 0.062, still worse than for Cobalt.

Finally, we end the selection of metals for the second electrode on Co; Gr; Fe; Mn; Cu.

The next step in materials selection process is to find an oxidizing agent. The guiding criteria is to achieve the largest difference in bonding energy of that agent to the selected metals per weight of the oxidizer. In rechargeable batteries, the products of electrode oxidation shall remain on electrodes for future reduction back to metals. In opposite case, the electrode material will be dispersed through the battery container and electrodes will vanish. So, the products of oxidation are crystals. In crystals, the major portion of ions bonding energy is between a positive metal ion and negative oxidizing ion. The value of this portion of bond energy is equal:

$$E_{bond} = n^2 e^2 K / (4 \pi e o (r+ \; + \; r-));$$
Eq.7

where e_o - dielectric constant of free space; r^+ - crystal radius of metal ion; r^- - c r y s t a l radius of oxidizing ion.

K is the coefficient associated with the bond type on the ionic-covalent scale. For purely ionic bond, K = 1. The bond is close to ionic when the difference in electronegativity between bonded ions is the largest. The electronegativity is the property of ions to attract additional electrons. Fluorine has the largest electronegativity value and alkali metals the lowest. Among the smallest and the lightest negative ions are N, O, OH, and F. The relevant data for those are given in Table 3.

TABLE 3
OXIDIZING AGENTS

Characteristic	N	O	OH	F
Mass	14	16	17	19
Valence	-3	-2	-1	-1
Electro-negativity	3.0	2.5	3.6	4.0
Covalent radius	3.75	0.73		0.71
Crystal radius	1.71	1.32	1.8	1.33

If all the selected oxidizing agents are to form purely ionic bonds with metals, then the best one will be N followed by O, F, and OH. This is true in relation to all of them but N which forms weaker covalent type bonds with metals. In order to evaluate all selected oxidizing agents in bonds with the selected metals, let's use the data on enthalpies of compounds.

The consolidated data on difference in enthalpies of different compounds of interest and there influence on the total cell reaction energy density are summarized in Table 4.

TABLE 4
CELL ENERGY DENSITIES

TABLE 4

CELL ENERGY DENSITIES

M_1 Ion	M_2 Ion	Oxid. Ion	Reaction	ΔH	ΔV	$\Delta V_{M1/M2}$	$\Delta V + \Delta V_{M1/M2}$	Me	E_{CR}	Priority
Al^{3+}	Co^{3+}	F^-	$Al + CoF_3 \leftrightarrow AlF_3 + Co$	124	-1.80	-2.09	-3.89	47.7	0.082	1
		OH^-	$Al + Co(OH)_3 \leftrightarrow Al(OH)_3 + Co$	127	-1.84	-2.09	-3.93	45.7	0.086	
		O^{2-}	$2Al + C_2O_3 \leftrightarrow Al_2O_3 + 2\,Cr$	126	-0.91	-2.09	-3.00	36.7	0.082	
Al^{3+}	Cr^{3+}	F^-	$Al + CrF_3 \leftrightarrow AlF_3 + Cr$	130	-1.88	-0.92	-2.80	45.3	0.060	
	Cr^{3+}	OH^-	$Al + Cr(OH)_3 \leftrightarrow Al(OH)_3 + Cr$	57	-0.82	-0.92	-1.74	43.3	0.040	
	Cr^{6+}	O^{2-}	$2Al + CrO_3 \leftrightarrow Al_2O_3 + Cr$	84	-0.61	-1.23	-1.84	25.7	0.072	
	Cr^{3+}	N^{3-}	$Al + CrN \leftrightarrow AlN + Co$	28	-0.40	-0.92	-1.32	31.0	0.042	
Al^{3+}	Fe^{3+}	F^-	$Al + FeF_3 \leftrightarrow Al\,F_3 + Fe$	68	-0.98	-1.62	-2.60	46.7	0.056	
		OH^-	$Al + Fe(OH)_3 \leftrightarrow Al\,F_3 + Fe$	107	-1.55	-1.62	-3.17	44.7	0.071	2
		O^{2-}	$2Al + Fe_2O_3 \leftrightarrow Al_2O_3 + 2\,Fe$	193	-1.40	-1.62	-3.02	35.7	0.085	
Al^{3+}	Mn^{3+}	F^-	$Al + MnF_3 \leftrightarrow Al\,F_3 + Mn$	8	-0.12	-1.48	-1.60	46.3	0.034	
		OH^-	$Al + Mn(OH)_3 \leftrightarrow Al(OH)_3 + Mn$	92	-1.33	-1.48	-1.60	46.3	0.063	
		O^{2-}	$2Al + Mn_2O_3 \leftrightarrow Al_2O_3 + 2\,Mn$	158	-1.14	-1.48	-2.62	35.3	0.074	4
Al^{3+}	Cu^{2+}	F^-	$2Al + 3Cu(OH)_2 \leftrightarrow 2Al(OH)_3 + 3Cu$	241	-1.74	-2.00	-3.74	60	0.062	
		OH^-	$2Al + 3CuO \leftrightarrow Al_2O_3 + 3Cu$	287	-2.06	-2.00	-4.06	58	0.070	
		O^{2-}	$2Al + 3CuO \leftrightarrow Al_2O_3 + 3Cu$	279	-2.01	-2.00	-4.01	49	0.082	3
	Cu^+	N^{3-}	$Al + Cu_3N \leftrightarrow AlN + 3Cu$	76	-1.10	-2.18	-3.28	77.7	0.042	

In the table, abbreviations stand for: ΔH - difference in enthalpies of products of the reaction, in Kcal/g-mole, ΔV - voltage potential due to that difference in enthalpy:

$$\Delta V = 0.0434\ \Delta H/n;\qquad\qquad\qquad\qquad\qquad\qquad Eq.8$$

$\Delta V_{M1/M2}$ - difference in voltage potential between electrode metals; M_e - gram equivalent weight of reactants; E_{cr} - relative cell energy density.

In this initial approach, let's make an assumption that all the problems of electrode kinetic are solved and all the above reactions can take place. The analysis of data in Table 4 shows that a) Fluorine is always worse than oxygen because of comparatively high gram-equivalent weight; b) Nitrogen bonds are the worst because of ionic weakness; c) the best oxidizing agent is Oxygen followed by hydroxide ion with a small margin; d) the best combinations of metals with oxygen and hydroxide differ in energy density from 0.086 to 0.070. From a system standpoint, they are all equal in performance. Four of the best reactions are marked in Table 4 with priorities. They involve four different metals: Co, Fe, Cu, and Mn.

In case of equal performance, the economic considerations start dictating our choices. Current commodity prices on the selected metals are given in Table 5.

TABLE 5
COST OF METALS

Metal	Price, $/LB
Fe	0.05
Al	0.52
Cu	0.87
Mn	1.43
Co	6.0
Pb	0.32

Comparing prices in Table 5 with our conclusions on energy density of reactions in Table 4, we can definitely select reactions between Al and Fe as our first choice, and Al and Cu as the second one. The oxidizing agents could be either Oxygen or hydroxide, almost without difference in performance.

Finally, it is interesting to compare the availability of selected materials on earth for projections of future prices. In Table 6, the data on their density in the earth crust are given.

TABLE 6
DENSITY OF ELEMENTS IN EARTH'S CRUST

Order Among All Elements	Element	Density in PPM
1	O	466,000
3	Al	81,300
4	Fe	50,000
25	Cu	70

It is encouragingly coincident that the three elements, Al, Fe, and O, which were selected for one of the most energy dense and economical electrochemical reaction, are among four of the most spread on earth (Si is #2).

The chemical reaction between iron oxide and aluminum actually takes place and the heat generated increases the temperature of the products above 1,000°C. This is widely used in welding as well as in ammunition, in substances used in Napalms.

CELL TYPE

In respect to chemical change of the cell materials, there could be three possible combinations shown in Table 7.

TABLE 7
CELL TYPES

Cell Type	First Electrode	Electrolyte	Second Electrode
A	Active	Inactive	Active
B	Active	Active	Inactive
C	Active	Active	Active

In the cell Type A, both electrodes undergo chemical change during cell operation, but not an electrolyte. In the cell Type B, only one of the electrodes is chemically inactive, and in the cell Type C all major cell components undergo chemical change.
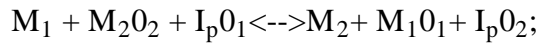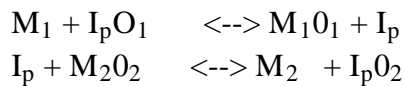
In A-Cell, the most energy dense reaction is like this:

$$M_1 + M_2 0 <--> M_2 + M_1 0$$
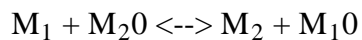
where - M_1; M_2 - electrode metals; O -oxidizing agent.

In B-Cell, in comparison with A-Cell, one of the electrodes is inactive and the electrolyte carries the function of the second electrode. The most energy dense reaction is the same as above, and $M_2 0$ is the initial electrolyte. One of the final products of reaction, metal M_2, will be dispersed in the cell container, as it doesn't have an electrode space according to a definition of B-Cell. For this reason, B-Cell is not rechargeable and is, therefore, not suitable for automotive applications.

In C-Cell, the most energy dense reactions between electrodes are like following:

$$M_1 + I_pO_1 \quad \longleftrightarrow \quad M_1O_1 + I_p$$
$$I_p + M_2O_2 \quad \longleftrightarrow \quad M_2 + I_pO_2$$

$$M_1 + M_2O_2 + I_pO_1 \longleftrightarrow M_2 + M_1O_1 + I_pO_2;$$

where: M_1 and M_2 - metals of electrodes; O_1 and O_2 - oxidizing agents;
Ip - positive ion of electrolyte.

Comparing this reaction with the first one, we can find that there is an additional source of energy - the electrolyte chemical change. This additional source might improve energy density. Because one of the positive ions in the reactions on electrodes doesn't have to be a metal, we can select the lightest one, Hydrogen. Now let's calculate if we can improve the energy density in C-Cell by doing so.

In Table 8, The results of such calculations are shown for the best possible combinations of metals and oxidizing agents.

TABLE 8
CELL REACTIONS

Type	Reaction							δH	δV	δM	E_{CR}
C	2 Al	+	$3H_2O$	$\leftrightarrow$	Al_2O_3	+	$6H^+$	-19	+0.14	9	0.052
	6 H^+	+	2 FeF_3	$\leftrightarrow$	2Fe	+	6 HF				
A	2 Al	+	Fe_2O_3	$\leftrightarrow$	Al_2O_3	+	Fe	0	0	0	0.085
C	2 Al	+	$3H_2O$	$\leftrightarrow$	Al_2O_3	+	$6H^+$				
	6 H^+	+	$3CuF_2$	$\leftrightarrow$	3Cu	+	6HF	0	0	20	0.058
A	2 Al	+	3CuO	$\leftrightarrow$	Al_2O_3	+	3Cu	0	0	0	0.082

In the table abbreviations stand for: dH - change in enthalpy in comparison with A-Cell reaction; dV - change in voltage in comparison with A-Cell reaction; dM - change in gram-equivalent weight in comparison with A-Cell; Ecr - relative cell energy density.
The calculations show that we always lose in gram-equivalent weight of reaction and never win in enthalpy. Besides that, C-Cell has disadvantages of electrolyte change, and, associated with it, changes in electrical conductivity, freezing point, electrode kinetics, etc. Usually those changes are compensated by surplus of electrolyte, which further diminishes the energy density.

In summary, the most energy dense reaction is the simplest one in A-Cell. This cell type A shall be utilized for automotive propulsion. The example of such a cell is the Edison (!) cell, or Ni-Fe cell, with KOH aqueous electrolyte. It is well known that electrolyte in the cell remains

almost without change during operation and the cell has excellent environmental and utilization characteristics.

AUTOMOBILE-BATTERY SYSTEM ANALYSIS

In order to study the practicality of use of even the most dense and economical batteries for automobile propulsion, let's make an assumption that the kinetics problems of chemical reactions in such batteries described above are resolved. Let's compare the newly devised battery cells with the existing ones to get a feeling of practically achievable energy densities in relation to the theoretical levels, and then compare all of them with the automobile energy requirements to look at economy of purely electric propulsion.

First, let's make a comparison of theoretical energy densities of the new cells with some existing ones. The results are shown in Table 9.

TABLE 9
THEORETICAL ENERGY DENSITIES OF CELLS

Reaction	Voltage V	Gram-Equiv.	Energy Density Wh/Kg
Lead-acid cell $Pb\ O_2 + 2H_2SO_4 + Pb \leftrightarrow$ $\quad\quad \leftrightarrow 2Pb\ SO_4 + 2H_2O$	2.04	321	170
Edison (Ni-Fe) cell $Fe + 2Ni\ OOH + 2H_2O \leftrightarrow$ $\quad\quad \leftrightarrow Fe(OH)_2 + 2Ni\ (OH)_2$	1.35	138	260
Ni-Zn cell $Zn + 2Ni\ OOH + 2H_2O \leftrightarrow$ $\quad\quad \leftrightarrow Zn(OH)_2 + 2Ni\ (OH)_2$	1.9	142	360
Zinc-Chlorine cell $Zn + (Cl_2 \times 8H_2O) \leftrightarrow$ $\quad\quad \leftrightarrow ZnCl_2 + 8H_2O$	2.1	136	410
Al-S cell $2\ AL + 3S + 3OH^- + 3H_2O \leftrightarrow$ $2Al\ (OH)_3 + 3HS^-$	1.3		910
Al-Fe-O $2Al + Fe_2O_3 \leftrightarrow Al_2O_3 + 2Fe$	3.02	35.7	2,270
Al-Cu-O $2Al + 3CuO \leftrightarrow Al_2O_3 + 3Cu$	4.01	49	2,190
Al-Fe-OH $Al + Fe(OH)_3 \leftrightarrow Al\ (OH)_3 + Fe$	3.17	44.7	1,900

From comparison, we can find that even the best cell under development now, Al-S, is 2.5 times lower in theoretical energy density than the cells described in this paper.

Now let's make a transition to practical energy densities which depend on usage of electrode materials, properties of materials, type of a cell, and associated with it the amount of electrolyte and construction overhead. The estimate of practical energy density in our batteries can be made on the basis of existing difference in practical and theoretical values for established technology batteries. In Table 10 below, the appropriate data are combined.

TABLE 10
EXPECTED PRACTICAL ENERGY DENSITIES

	Battery	Energy Densities in Wh/kg			
		Theoretical	Current	Projection	Ratio
	Existing				
1	Lead-Acid	170	40	50	3.4
2	Edison, Ni-Fe	260	50	60	4.4
3	Ni-Zn	360	60	70	5.1
4	Zn-Cl	410	70	80	5.2
	USABC Goals				
	Mid-term			80	
	Long-Term			200	
	Proposed				
1	Al-Fe-O	2,270		450	5
2	Al-Cu-O	2,190		440	5
3	Al-Fe-OH	1,900		380	5

The proposed batteries are close to Edison batteries in usage of materials and their properties as well as in composition of electrolyte and its usage. We can make a conservative estimate that the practical ratio of theoretical and projected energy densities is 5.

Then, we shall expect the energy density from the cells described in this paper in the range of 380-450 Wh/kg. This is favorably comparable with the long term goals of USABC United States Advanced Battery Consortium) of only 200 Wh/kg

Characteristic	U/M	93' Ford Escort GT	93' Old Cutlass Cierra	93' Chrys. New Yorker
Weight with one passenger, no cargo	lbs.	2,600	3,060	3,800
Tires rolling friction coefficient		0.012	0.010	0.009
Frontal area	m2	2.26	2.43	2.67
Drag coefficient		0.34	0.33	0.34
Speed	Mi/h	65	65	65
Inertia power portion on FHWC	%	17	20	25
Rolling resistance power	kW	3.9	3.9	4.3
Airdynamic drag power (no wind)	kW	11.3	12.1	13.7
Positive part of inertia power	kW	2.6	3.2	4.5
TOTAL POWER	kW	17.8	19.1	22.5
Drive train efficiency	%	90	90	90
Power of the power plant	KW	19.8	21.2	25.0
Minimum driving range	Mi	200	200	200
Minimum energy needs	KWh	61	65	77
Motor and converter efficiency	%	80	80	80
Electric energy output	kWh	76	82	96
Maximum battery depletion		0.7	0.7	0.7
Battery energy capacity, 3 hours rate	kWh	109	116	137

.

Now, let's determine the weight of the new imaginary batteries required to satisfy the energy needs of different automobiles in common use. One of the most common driving conditions is along the level road at more or less constant speed. Let's assume that this speed is equal to 65 Mi/h, maximum allowed by law.

In case of a level road, there are three forces acting upon the automobile: rolling resistance, aerodynamic drag, and inertia force experienced during acceleration and deceleration.

The power to overcome the rolling resistance is equal $P_R = W*f*V$, where W - weight of the automobile; V - speed; f - tires rolling friction.

The power to overcome the aerodynamic drag is equal to $P_D = 13.10^{-6}C_WAV^3$, where CW - drag coefficient; A - frontal area, m^2; V - speed, mph.

The power to overcome inertia can be found in statistical data on driving patterns. No exclusion is made on usage of regenerative braking which, at best, can save approximately 20-30% of this portion of drive power during highway cruising.

TABLE 11
ENERGY REQUIREMENTS OF ELECTRIC AUTOMOBILES

Characteristic	U/M	93' Ford Escort GT	93' Old Cutlass Cierra	93' Chrys. New Yorker
Weight with one passenger, no cargo	lbs.	2,600	3,060	3,800
Tires rolling friction coefficient		0.012	0.010	0.009
Frontal area	m2	2.26	2.43	2.67
Drag coefficient		0.34	0.33	0.34
Speed	Mi/h	65	65	65
Inertia power portion on FHWC	%	17	20	25
Rolling resistance power	kW	3.9	3.9	4.3
Airdynamic drag power (no wind)	kW	11.3	12.1	13.7
Positive part of inertia power	kW	2.6	3.2	4.5
TOTAL POWER	kW	17.8	19.1	22.5
Drive train efficiency	%	90	90	90
Power of the power plant	KW	19.8	21.2	25.0
Minimum driving range	Mi	200	200	200
Minimum energy needs	KWh	61	65	77
Motor and converter efficiency	%	80	80	80
Electric energy output	kWh	76	82	96
Maximum battery depletion		0.7	0.7	0.7
Battery energy capacity, 3 hours rate	kWh	109	116	137

In Table 11, the summary of calculations for three different 1993 production model of automobiles is shown, if they were to be powered by the electric power plants. The technical data

for such automobiles were provided by the manufacturers. The inertia portion of the total power was determined as a percentage of the sum of rolling power and airdynamic drag power on EPA Federal Highway Cycle (FHWC).

We assumed that the drive train efficiency from the motor to the driving wheels is at least 0.9 which is quite optimistic.

We selected the lowest marketable driving range of 200 miles which is still quite inadequate in comparison with 400 miles for gasoline powered cars.

The electric motor and power converter efficiency was assumed to be over 80% which is also optimistic.

We selected the battery charge depletion level of 70% versus maximum rated 80% to assure more reasonable cycle life.

The algorithm of calculations is quite self-evident. The results for the batteries energy capacities as measured on 3 hours discharge cycle are shown on the bottom line. They vary from 109 kWh for a small car like Ford's Escort to 137 kWh for a full size car like Chrysler's New Yorker.

At this time, it is important to look at the desired rate of battery charging from the user viewpoint. Because we have limited the range to 200 miles, we should expect to recharge the battery fast and along the highway. Currently, it takes maybe a minute to do so. As we like to preserve this fast "refuelling" time, then the charge rate for the battery in "New Yorker" will be 137*60=8.22 megaWatt (!). What if there are 6 cars at the recharge station at the same time ? Then the station's electrical service shall carry at least 50 megaWatt of power. And we shall have twice as many stations because the driving range is limited to 200 miles versus currently common 400 miles.

Now, let's find out what is the expected weight of the existing batteries and the ones described in this paper to satisfy energy requirements of different automobiles. The results of the calculations of expected battery weights are summarized in Table 12.

TABLE 12
WEIGHTS OF THE BATTERIES, LBS.

Characteristic	U/M	93' Ford Escort GT	93' Old Cutlass Cierra	93' Chrys. New Yorker
Battery Energy, KWH	kWh	109	116	137
Battery weight: Lead-Acid Edison's,Ni-Fe Ni-Zn Zn-Cl	lbs	5,983 4,786 3,988 3,419	6,414 5,131 4,276 3,665	7,560 6,048 5,040 4,320
Proposed batteries, at 450 Wh/kg	lbs.	532	570	672

As we see, the weight of all existing batteries or the ones under development exceeds significantly the weight of the car they are supposed to propel. It means that none of such batteries can power even itself under conditions described in Table 11, which is to drive an off-the-shelf automobile for 200 miles at average speed of 65 Mi/h on level road.

The possible batteries described in this paper will allow driving because their projected weight is lower than the automobile weight. Now we need to make a correction on the battery weight which will enable to carry the energy for driving this battery as a cargo. For estimate purposes, let's assume that the electric power plant has the same weight as a mechanical one and that the battery weight comes as a pure addition to the automobile gross weight. Let's further assume that the total power requirements are increasing somewhat proportional to the gross weight. Then the formula to calculate the total battery weight will be as follows:

$$W_b = W_{b0} * W_c / (W_c - W_{b0}); \hspace{4cm} Eq.9$$

where W_b - battery weight in the automobile; W_c - automobile weight without the battery; W_{b0} - battery weight necessary to drive the car without the battery itself.

Eq. 9 vividly shows that when the battery weight necessary to propel the car is equal or exceeds the net car weight, the very idea of building an electric car becomes mute due to an infinite battery weight requirement.

The weights of the possible batteries described in this paper, in the automobiles taken as an example, and enabling the driving under conditions presented in Table 11 are shown in Table 13.

TABLE 13
WEIGHTS OF THE ENERGY DENSE BATTERIES, LBS.

Battery	Energy Density	93' Ford Escort GT		93' Olds Cutlass Cierra		93' Chrysler New Yorker	
	Wh/kg	Battery	Car+Bat.	Battery	Car+Bat.	Battery	Car+Bat.
Al-Fe-O	450	669	3,269	701	3,761	816	4,616
Al-Cu-O	440	777	3,377	812	3,872	944	4,744
Al-Fe-OH	380	831	3,431	866	3,926	1,007	4,807

The described possible batteries will add approximately 25% to the weight of the car, but they will be able to perform the function.

Finally, let's estimate the economics of such imaginary batteries. Existing lead-acid SLI battery can serve as a benchmark of a low cost battery. The current retail cost for such batteries is approximately $50 for 25 lbs. battery or $2/lb. The most expensive material in this battery is Lead which has current commodity cost of $0.32/lb. (Table 5). Then, the ratio of such commodity cost to the user retail cost is approximately six (6). If we can forecast that Aluminum-Iron battery can be built, and also its manufacturing technology will be similar to the lead-acid one, then we might expect the user cost also be six times larger than the cost of the most expensive material, Aluminum. We shall expect then the user cost of $0.52 * 6 = $3.12/lb.

COMPARATIVE ENERGY ECONOMICS OF ELECTRIC PROPULSION

Earlier in the paper, we have looked at practically the most economical solution for purely electric propulsion, from energy storage viewpoint. Now, let's compare this solution with two existing ones based on combustible fuels. The first one is a most common solution using gasoline, and the other one - using an ethanol as a renewable fuel.

In Table 14, we summarized the data necessary for evaluation of comparative economics.

TABLE 14
COMPARATIVE ENERGY ECONOMICS

Characteristic	U/M	Gasoline	Ethanol	Al-Fe-O Battery
Weight with one passenger, no cargo	lbs.	3,800	3,800	4,616
Battery energy use for 200 Mi at 65 Mi/h	kWh			120
Fuel economy	Mi/gal.	24	16	
Amount of fuel	gal.	8.3	12.5	
Cost of fuel	$	10.4	15.5	
Cost of electricity, at 8 c/kWh	$			9.6
Yearly fuel cost for 14,000 Mi	$	729	1,085	672
Yearly electric energy user cost benefit	$	57	413	

We have compared the annual fuel cost for three alternatives. In all three cases, we used Chrysler's New Yorker as a base vehicle.

In case of gasoline, the car's fuel economy is approximately 24 Mi/gal under driving conditions considered; recent cost of gasoline is $1.25/gal. on average.

In case of ethanol, we assumed that the fuel economy will be 1.5 times lower in comparison with gasoline which is without taking into consideration 30% increase in fuel efficiency in vehicles specifically designed for ethanol; and that the retail price is $1.25/gal.

In case of electric energy, we assumed the electricity cost of 8 cents per kWh what is quite favorable in comparison with 9.7 cents currently charged by Potomac Electric power company.

Further, we accepted 14,000 miles average annual driving distance used nationally in evaluation of user behavior.

Under such input, the annual costs for energy is as shown in the Table 14. The first striking discovery is that the current gasoline cost and electric energy cost are almost the same, $57 per year difference, which is trivial. It means that such electric car can compete with a gasoline powered car only on the initial price. Then, the cost of the electric power plant consisting of an electric motor, an inverter, and this battery shall be no more than the cost of the gasoline power plant consisting of the engine and transmission.

The other argument is for a quite remote future when oil reserves on earth will be so depleted that the gasoline prices will become very high. Then, we can compare economics of ethanol as a renewable fuel with the electricity as a source of primary energy in the automobile itself, without the cost of generating this electricity. In our example, the cost of ethanol exceeds the cost of electricity by $413 a year (if electricity cost in this remote future will be the same as it is today - ?). This amount does not change much the economics of the electric power plant.

It is also quite clear that the operating life of the battery itself shall be long enough so its amortization cost will be small in comparison with the energy cost, like 1/3 of the annual electricity cost. In our example it will be approximately $224/year. If the battery cost will be $2,547 (816 lbs. at $3.12/lb.) and annual amortization $224, then operating life shall be over 11 years, practically equal to the operating life of a vehicle.

CONCLUSION

Let's summarize our assumptions and create directions for the future research.

- We assume that the most energy dense, from physics standpoint, reaction in the battery cell which is based on Oxygen exchange between Aluminum and Iron can provide energy density of 450 Wh/kg during 3 hours discharge, over 2 times higher than the long term goal of USABC
- We recognize that such battery materials are ones of the lowest cost
- We assume that we can overcome the kinetics problems of such reaction making it reversible, or battery - rechargeable
- We assume that we can overcome the safety problems associated with handling of hundreds of pounds of such material, which is like Napahm, during crashes

•We assume that we can overcome the limitations of a cycle life and make new batteries last for at least 10 years
•We will limit the driving range on the highway to 200 miles, a half of customary range, and consumers will accept it
•We assume that there will be a network of recharge stations twice as dense as currently practiced and that each station will have an electric service with 50 megaWatts of capacity or more
•We assume that the cost of the electric driveline including the battery will be no more than the cost of a gasoline based driveline

Only if all of the above assumptions will materialize, we can expect to see that an electric battery can substitute combustible fuels like gasoline, ethanol, etc. as a source of energy for automobile propulsion. Common sense tells us that in the foreseeable future and beyond, the electric energy storage in the batteries will not substitute energy carriers as gasoline, or even ethanol, as a competing technology.

Then, the question is are there any uses of the batteries for automobiles ? Below, we summarize the direction for major future studies aimed on creation of such uses.

First, the batteries have already proved themselves as an excellent source of power (!) to start the engine in the automobile. We shall build on this strength and extend the application to both starting and accelerating the vehicle rather than just an engine. This will be an application in a specific category of hybrid-electric power plants in which an electric part of the plant assists the engine in starting and accelerating the vehicle. In such application, the power density is much more important than the energy density. Further study is required for the MOST POWER DENSE AND MORE ECONOMICAL BATTERIES.

The engine in a hybrid-electric power plant can be downsized without deteriorating the vehicle performance which leads to much better utilization efficiency of the mechanical energy generated by this engine, two times or more.

Second, in hybrid-electric drives, batteries will be subjected not to deep and infrequent discharges but to shallow and frequent ones. Further study is required of the thermodynamics of reversible battery reactions to find the processes leading to long operating life under such conditions.

Another major area of research shall focus on manufacturing processes for the existing and to be discovered batteries allowing to connect individual cells in long strings for high voltage applications, without deterioration of the operating life under frequent charge and discharge cycles.

And finally, the detailed study of chemical bonds in fuels and in electrochemical reactions can be useful to establish the theoretical limits by comparing the energy in Hydrogen and Carbon bonds in fuels versus Oxygen and similar bonds in electrochemical reactions.

The research outlined above shall lead to fulfillment of the intuitive expectations that the electrical engineering technology shall solve the problems of mechanical engineering technology of automobiles. If this paper will stimulate such research, the author will be more than gratified.

MAIN REFERENCES

1   Handbook of Chemistry and Physics, 58th edition, CRC Press, Cleveland, 1977
2   Automotive Handbook, 18th edition, Bosch.
3.   G. W. Vinal, Storage Batteries, 4th edition, John Wiley & Sons, 1982
4.   C.L. Gray, F. von Hipple, The fuel Economy of LightVehicles, Scientific American,
         v.244, May 1981
5.   R.U. Ayres, R.P. McKenna, Alternatives to the Internal Combustion Engine,
         Johns Hopkins University, Baltimore, 1972
6.   Automotive fuel Economy, part 2, SAE, 1979
7.   P.M. Heldt, High-Speed Combustion Engines, 14th edition, NY A CK, N. Y., 1948
8.   Ford Motor Co., The Automobile as an Energy Converter, Technology Review, 2, 1975
9.   Numerous publications of the Department of Energy, Electric and Hybrid
         Vehicle Programs
10.   Selected U.S. Patents in the battery technology field: 3,993,502; 4,086,363; 4,146,680;
          4,149,953
11.   D. Peramunage and S. Licht, A Solid Sulfur Cathode for Aqueous Batteries, Science,
         Vol. 261, August 20, 1993
12.   United States Advanced Battery Consortium, Contractor's Coordination Meeting,
         October 28, 1991.