

IEEE Catalog No.
83 CH1900-0



Conference Record

Industry

Applications

Society

IEEE-IAS-1983 Annual Meeting

1983

Papers Presented at the Eighteenth Annual Meeting
Sheraton Maria Isabel Hotel
October 3-7

Sponsored by the
IEEE Industry Applications Society

Library of Congress No. 80-640527

BATTERY VIABILITY IN AUTOMOBILE PROPULSION
(SYSTEM STUDY)

ALEX SEVERINSKY
IEEE Member, Ph.D., P. E.
Richardson, Texas

ABSTRACT

Electro-chemical theoretical limits on energy density in the storage batteries are presented. Comparison to passenger automobile requirements is made. Negative conclusion on the battery viability is derived at.

INTRODUCTION

In the last decade numerous attempts were made to develop electric cars with rechargeable batteries as an alternative automotive system. Despite considerable investment, all those attempts have failed.

This paper presents theoretical limits on energy density in practical batteries, describes several of the most energy dense batteries possible in a new combination of materials and construction, and compares those with other alternatives for automotive propulsion.

The material is presented in the following order: battery definition, physics of the battery processes, analysis of materials, cell type analysis, system analysis, alternatives, and conclusion.

DEFINITION OF THE BATTERY

We will define the battery from historical retrospective in relation to its application in automobiles as a practical energy source.

Constructionwise, the battery consists of several electro-chemical cells connected in series and/or in parallel. A cell contains, as minimum, two metal electrodes to conduct electric current and 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 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 -40°C to $+85^{\circ}\text{C}$. 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.

We will use this definition of the battery during the finding of the most energy dense combination of materials, processes and structures for it, because energy density characteristic is the most crucial in automotive propulsion.

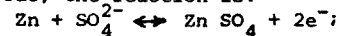
PHYSICS OF ELECTRO-CHEMICAL PROCESSES

The main phenomena which determines the energy transformation in electro-chemical processes is the difference in electron bonding energy (work function) in two different metals. When we bring them in contact, there appears the voltage potential across the contact due to that difference. 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 cancelling 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.

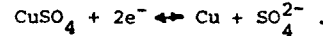
This is a well-known thermo-electric effect.

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. The whole process is called 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. Electrolytes are separated with the membrane permeable for SO_4^{2-} ions. On Zn electrode, the reaction is:



and on Cu electrode:



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 the zinc sulfate electrolyte and Cu ions in the copper sulfate electrolyte and in the metal. 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.

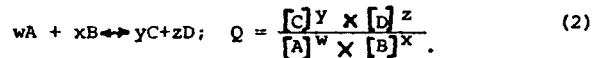
The ionic bonding energy of metal compounds in the solution depends on density of other ions or on concentration.

The relation between the cell voltage and concentration of ions in electrolyte was found by Nernst:

$$V = V_0 - \frac{RT}{nF} \ln Q, \quad (1)$$

where: V - actual cell potential; V_0 - 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 the generalized cell reaction



In practice, the concentration influence is usually very small as the value

$$\frac{RT}{F \cdot \log e} \approx 0.06 \text{ V}. \quad (3)$$

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 ionically 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) 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:

$$\frac{\Delta H}{nF} = v - T \frac{dv}{dT} \quad (4)$$

where ΔH - change in enthalpy.

Theoretical energy efficiency of the cell can be found by correction on the change in entropy or by using equation (5) 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 entropies is negligible for all practical purposes, the temperature coefficient is close to zero, and the cell thermodynamic efficiency is close to 100%.

ANALYSIS OF MATERIALS

We will base the analysis of materials on the physics of the cell and aim it at achievement of maximum energy density per weight of materials, the main characteristic of the battery for automotive propulsion.

The most important materials in the cell are electrode metals. We will begin analysis from elementary metals and then try to improve the results if possible at all. 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 of the list of reduction potentials are given in Table 1. There are shown metals with the highest energy density, and those are the lightest ones, as well as metals with the largest positive potential necessary for further analysis. In some cases, the reduction potential was calculated in the following way.

TABLE 1
METAL ENERGY DENSITIES

ATOMIC NUMBER	REACTION	Vo	M	Eo
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

If, for example: Fe³⁺ $\xrightarrow{+0.77V}$ Fe²⁺ $\xrightarrow{-0.44V}$ Fe,

$$\text{then } V_{Fe^{3+}/Fe} = \frac{+0.77 \times 1 + 2(-0.44)}{2 + 1} = -0.036V;$$

because energies add up in both reactions. The energy density Eo is defined like $E_o = \frac{V_o}{M/n}$ where M - atomic mass; n - valence.

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 due to larger ion radii and increase of atomic mass. 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, and 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 very toxic at the same time. The double advantage in energy density possessed by Be can not be economically justified. So, Al is our best choice for one of the cell electrodes from system standpoint.

Now, let's see if there is any intermetallic compound which might be better than Al. 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 $F_r \approx (ne)^2/r$; where 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 bonding. The potential we hope to achieve, even without counting on large molecular size, is the one possessed by Li. The mass of Al-Be compound is 36, so the expected $E_o \sim 0.083$. It is even worse than in any metal of the compound as majority of their energy carrying bonds are not used. Finally, Al is our best choice for the first electrode. Al - #1.

The selection of the second electrode is not as free as before; it is interdependent with Al energy density characteristic. 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:

$$E_{oM1/M2} = (E_{oM1}M_{1e} + E_{oM2}M_{2e}) / (M_{1e} + M_{2e}); \quad (5)$$

where Eo - energy densities; M1e, M2e - gram-equivalent of atom. Substituting the data for Al, we arrive at:

$$E_{oAl/M} = (1.66 + V_{oM}) / (9 + M_e). \quad (9)$$

TABLE 2

ATOMIC NUMBER	REACTION	VoM	Me = $\frac{M}{n}$	EoAl/M	PRIOR-ITY
23	V ²⁺ + 2e ⁻ ↔ V	-1.2	25.5	0.013	
24	Cr ³⁺ + 3e ⁻ ↔ Cr	-0.74	17.3	0.035	
24	Cr + 6e ⁻ ↔ Cr	-0.43	8.7	0.070	2
25	Mn ²⁺ + 2e ⁻ ↔ Mn	-1.03	27.5	0.017	
25	Mn ³⁺ + 3e ⁻ ↔ Mn	-0.18	18.3	0.054	4
26	Fe ³⁺ + 3e ⁻ ↔ Fe	-0.036	18.7	0.059	3
27	Co ²⁺ + 2e ⁻ ↔ Co	-0.28	29.5	0.036	
27	Co ³⁺ + 3e ⁻ ↔ Co	+0.43	19.7	0.073	1
28	Ni ²⁺ + 2e ⁻ ↔ Ni	-0.25	29.5	0.037	
29	Cu + e ⁻ ↔ Cu	+0.52	64	0.030	
29	Cu ²⁺ + 2e ⁻ ↔ Cu	+0.34	32	0.049	5
30	Zn ²⁺ + 2e ⁻ ↔ Zn	-0.76	32.5	0.022	
31	Ga ³⁺ + 3e ⁻ ↔ Ga	-0.56	23.3	0.034	
46	Pd ²⁺ + 2e ⁻ ↔ Pd	+0.83	53	0.040	
47	Ag ⁺ + e ⁻ ↔ Ag	+0.80	108	0.021	
78	Pt ²⁺ + 2e ⁻ ↔ Pt	+1.2	97.5	0.027	
79	Au ³⁺ + 3e ⁻ ↔ Au	-1.42	65.7	0.041	
80	Hg ²⁺ + 2e ⁻ ↔ Hg	+0.85	100.5	0.023	

The results of calculation for Eo Al/M for the number of the best combinations are shown in Table 2.

The data show that our best matching metals with Al are in order Co³⁺; Cr⁶⁺; Fe³⁺; Mn³⁺; and Cu²⁺. 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 viewpoint. So their use is restricted primarily not by cost but by lower technical characteristics.

Now it's again the time to analyze if we might 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 Co. Let's imagine even impossible that two light transition metals with average atomic mass of 60 each are inert as gold in intermetallic compound, so the potential is ~1.4V, and valence is 3. Then Eo Al/M will be 0.062, still worse than for Co.

Finally, we stop 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 oxidization shall remain on electrodes for future reduction back to metals. In the opposite case, the electrode material will be dispersed through the battery container and electrodes will vanish. So, the products of oxidization are crystals. In crystals, the major portion of ions bonding energy is between a positive metal ion and a negative oxidizing ion. The value of this portion of bond energy is equal

$$E_{\text{bond}} = \frac{n^2 e^2 K}{4\pi \epsilon_0 (r^+ + r^-)} \quad (6)$$

where ϵ_0 - dielectric constant of free space; r^+ - crystal radius of metal ion; r^- crystal 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 one 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	0.75	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 those oxidizing agents in bonds with the selected metals, it is better to look in the tables of heat of formation of compounds. Those data include not only single bond energies but energies of all other bonds to the solid body.

The consolidated data on difference in enthalpies of different compounds of interest and their influence on the total cell reaction energy density is gathered in Table 4. In the table, abbreviations stand for:

ΔH_o - difference in enthalpy of products of the reaction,

ΔV - voltage potential due to that difference in enthalpy

$$V [v] = \frac{0.0434 \Delta H;}{n} \quad (7)$$

where n - total number of transported electrons; VML/M2 - difference in voltage potential between electrode metals; Me - gram equivalent weight of reactants; $E_{\text{cell}} = \frac{V}{Me}$ - overall cell energy density:

At this level of study let's make an assumption that all the problems of electrode kinetics are solved and all the above reactions 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 weakness; c) the best oxidizing agent is oxygen followed by hydroxide ion with the 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 economical considerations start dictating our choice. Current commodity prices on those metals and aluminum are given in Table 5.

TABLE 5
COST OF METALS

METAL	PRICE, \$/LB
Fe	0.25
Al	0.5
Cu	0.7
Mn	3.0
Co	6.0

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 oxygen or hydroxide almost without difference in performance.

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

TABLE 6

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, we selected for one of the most energy dense electro-chemical 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.

CELL TYPE

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

TABLE 4
CELL ENERGY DENSITIES

M ₁ ion	M ₂ ion	Oxid. ion	Reaction	Kcal/g-mole	ΔH_0	ΔV	V	M1/M2	V = V + V _{M1/M2}	Me _x = $\sum M_i/M_i$	E _{cell}	Priority
Al ³⁺	Co ³⁺	F ⁻	Al + CoF ₃ ↔ AlF ₃ + Co	124	-1.80	-2.09			-3.89	47.7	0.082	
		OH ⁻	Al + Co(OH) ₃ ↔ Al(OH) ₃ + Co	127	-1.84	-2.09			-3.93	45.7	0.086	1
		O ²⁻	2Al + Co ₂ O ₃ ↔ Al ₂ O ₃ + 2 Co	126	-0.91	-2.09			-3.00	36.7	0.082	
Al ³⁺	Cr ³⁺	F ⁻	Al + CrF ₃ ↔ AlF ₃ + Cr	130	-1.88	-0.92			-2.80	45.3	0.060	
		OH ⁻	Al + Cr(OH) ₃ ↔ Al(OH) ₃ + Cr	57	-0.82	-0.92			-1.74	43.3	0.040	
		Cr ³⁺	Al + Cr(OH) ₃ ↔ Al(OH) ₃ + Cr	84	-0.61	-1.23			-1.84	25.7	0.072	
		Cr ⁶⁺	2Al + CrO ₃ ↔ Al ₂ O ₃ + Cr	28	-0.40	-0.92			-1.32	31.0	0.042	
Al ³⁺	Fe ³⁺	N ³⁻	Al + CrN ↔ AlN + Cr	28	-0.40	-0.92			-1.32	31.0	0.042	
		F ⁻	Al + Fe F ₃ ↔ Al F ₃ + Fe	68	-0.98	-1.62			-2.60	46.7	0.056	
		OH ⁻	Al + Fe(OH) ₃ ↔ Al F ₃ + Fe	107	-1.55	-1.62			-3.17	44.7	0.071	
Al ³⁺	Mn ³⁺	O ²⁻	2Al + Fe ₂ O ₃ ↔ Al ₂ O ₃ + 2Fe	193	-1.40	-1.62			-3.02	35.7	0.085	2
		F ⁻	Al + MnF ₃ ↔ Al F ₃ + Mn	8	-0.12	-1.48			-1.60	46.3	0.034	
		OH ⁻	Al + Mn(OH) ₃ ↔ Al(OH) ₃ + Mn	92	-1.33	-1.48			-1.60	46.3	0.063	
Al ³⁺	Cu ²⁺	O ²⁻	2Al + Mn ₂ O ₃ ↔ Al ₂ O ₃ + 2Mn	158	-1.14	-1.48			-2.62	35.3	0.074	4
		F ⁻	2Al + 3Cu(OH) ₂ ↔ 2Al(OH) ₃ + 3Cu	241	-1.74	-2.00			-3.74	60	0.062	
		OH ⁻	2Al + 3CuO ↔ Al ₂ O ₃ + 3Cu	287	-2.06	-2.00			-4.06	58	0.070	
		O ²⁻	2Al + 3CuO ↔ Al ₂ O ₃ + 3Cu	279	-2.01	-2.00			-4.01	49	0.082	3
	Cu ⁺	N ³⁻	Al + Cu ₃ N ↔ AlN + 3 Cu	76	-1.10	-2.18			-3.28	77.7	0.042	

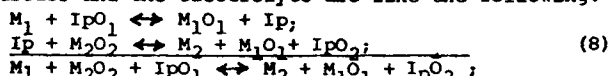
TABLE 7
CELL TYPES

CELL TYPE	FIRST ELECTRODE	ELECTROLYTE	SECOND ELECTRODE
A	active	inactive	active
B	active	active	inactive
C	active	active	active

In A-Cell, the most energy dense reaction is like this; $M_1 + M_2O \leftrightarrow M_2 + M_1O$, where -M₁ and M₂ - 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 that electrode. The most energy dense reaction is the same as above, and M₂O is the initial electrolyte. One of the final products of reaction, M₂, will be dispersed in the cell container, as it doesn't have electrode space according to a definition of B-Cell. For this reason, B-Cell is not rechargeable.

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



where: M₁ and M₂ - metal electrodes; O₁ and O₂ - oxidizing agents; Ip - positive ion of electrolyte.

Comparing this reaction with the first one, we find that there is an additional source of energy - the electrolyte chemical change. This additional source might improve energy density only if the reactions on electrodes are more energy dense. 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. In the table abbreviations stand for:

ΔH - change in enthalpy in comparison with A-Cell reaction; ΔV - change in voltage in comparison with A-Cell potential; ΔM - change in gram-equivalent weight in comparison with A-Cell; E_x - energy density.

The calculations show that we always lose in gram-equivalent weight of reaction and never win in enthalpy. So, the most energy dense reaction is the simplest one in A-Cell. Besides that, C-Cell had disadvantages of electrolyte change, and, associated with it, changes in electrical conductivity, freezing point, electrode kinetics, et cetera. Usually those changes are compen-

sated by surplus of electrolyte, which further diminishes the energy density.

TABLE 8
CELL REACTIONS

TYPE	REACTION	ΔH	ΔV	ΔM	E _x
C	2 Al + 3H ₂ O ↔ Al ₂ O ₃ + 6H ⁺	-19	+0.14	9	0.052
	6 H ⁺ + 2 FeF ₃ ↔ 2Fe + 6 HF				
A	2 Al + Fe ₂ O ₃ ↔ Al ₂ O ₃ + Fe	0		0	0.085
C	2 Al + 3H ₂ O ↔ Al ₂ O ₃ + 6H ⁺				
	6 H ⁺ + 3CuF ₂ ↔ 3 Cu + 6HF	0		0	0.058
A	2 Al + 3CuO ↔ Al ₂ O ₃ + 3Cu	0		0	0.082

The 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 overall has excellent environmental and utilization characteristics.

SYSTEM ANALYSIS

At this stage of study of battery viability for automobile propulsion, let's make an assumption that the kinetics problems of chemical reactions in practically the most energy dense batteries described above are solved. Now we would like to know how economical those batteries could be to determine if we are to pursue this development further. We will compare our batteries 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 our cells with some existing ones to get a feeling of where do we stand. The results are shown in Table 9.

From comparison we find that the best cells under intensive development now, Ni-Zn and Zn-Cl, are 5 to 7 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 could be made on the basis of existing difference in practical and theoretical values for similar

batteries.

TABLE 9
THEORETICAL ENERGY DENSITIES OF CELLS

REACTION	VOLTAGE V	GRAM- EQUIV.	ENERGY DEN.Wh/kg
Lead-acid cell $Pb O_2 + 2H_2SO_4 + Pb \leftrightarrow$ $\leftrightarrow 2Pb SO_4 + 2H_2O$	2.04	321	170
Edison(Ni-Fe) cell $Fe + 2Ni OOH + 2H_2O \leftrightarrow$ $\leftrightarrow Fe(OH)_2 + 2Ni(OH)_2$	1.35	138	260
Ni-Zn cell $Zn + 2NiOOH + 2H_2O \leftrightarrow$ $\leftrightarrow Zn(OH)_2 + 2 Ni(OH)_2$	1.9	142	360
Zinc-Chlorine cell $Zn + (Cl_2 \times 8H_2O) \leftrightarrow$ $\leftrightarrow ZnCl_2 + 8H_2O$	2.1	136	410
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

In Table 10 below, the appropriate data are combined.

TABLE 10

BATTERY	ENERGY DENSITIES IN Wh/kg			
	Theoret.	Current	Projection	Ratio
<u>Existing</u>				
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
<u>Proposed</u>				
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. The conservative estimate is made, that the practical ratio of theoretical and projected energy densities is 5.

Now we are ready to compare practically achievable energy densities in batteries with actual automobile requirements. In case of level road, there are three forces acting upon the automobile: rolling resistance, aerodynamic drag, and inertia force experienced during acceleration. The power to overcome the rolling resistance is equal $P_R = WfV$, where W - weight of the automobile; V - speed; f - tire rolling friction.

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

The power to overcome inertia could be found in statistical data on driving patterns; no exclusion is made on usage of regenerative braking which, at best, can save 50% of this portion of drive power.

In Table 11 the summary of calculations of automobiles energy requirements driven by purely electric system, is given. There was selected the lowest

marketable driving range of 200 miles while still being unfavorably comparable with 400-500 miles for existing cars. The maximum speed limit was selected because the highest power demand is at the highest speed due to quadratic increase in aerodynamic drag force. The battery depletion coefficient was selected based on the best results achieved in existing batteries to have long cycle life.

TABLE 11
ELECTRIC AUTOMOBILE ENERGY REQUIREMENTS

CHARACTERISTIC	MID-SIZE CAR	COMPACT	SUB- COMPACT
Net weight, lbs	3,500	2,700	2,000
Load, lbs	500	500	500
Total weight, lbs	4,000	3,200	2,500
Radial-tire rolling friction	0.015	0.015	0.016
Frontal area, m^2	2.0	1.85	1.7
Drag coefficient	0.5	0.4	0.45
Speed, mph	55	55	55
Rolling resistance power, kW	6.5	5.2	4.3
Drag power (no wind), kW	8.8	6.5	6.7
Inertia power, kW	8	6	5
Total power, kW	23	18	16
Drive train efficiency	0.9	0.9	0.9
Propulsion power, kW	26	20	19
Minimum drive range, mi	200	200	200
Minimum energy, kWh	100	75	70
Motor and converter efficiency	0.85	0.82	0.8
Battery energy out, kWh	120	90	85
Maximum battery depletion	0.7	0.7	0.7
Total battery energy capacity, kWh	170	130	120

Now let's see how existing batteries and proposed ones can satisfy different car energy requirements. The results of the calculations of expected battery weights are summarized in Table 12.

TABLE 12
BATTERIES WEIGHT, LBS

CAR TYPE	MID-SIZE	COMPACT	SUB- COMPACT
Battery Energy, KWH	170	130	120
Battery:			
Lead-Acid	7,500	5,700	5,300
Ni-Fe	6,200	4,800	4,400
Ni-Zn	5,300	4,100	3,800
Zn-Cl	4,700	3,600	3,300
Proposed batteries, 400 Wh/Kg on average	940	720	660

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. Let's make a correction on additional battery weight to provide the energy to carry the battery itself. For simplicity, the assumption of equivalent increase with weight in all power components could be made. Then the formula to calculate the total battery weight will be as follows:

$$E_x (1 + W_B/W_C) = E_B W_B \quad (9)$$

where E_x - total battery energy in the car without battery addition; W_B - battery weight; W_C - car weight; E_B - battery energy density.

From that formula we easily derive:

$$W_B = 1 / (1/W_{B0} - 1/W_C) \quad (10)$$

where W_{B0} - battery weight necessary to drive the car without the battery itself, Table 12.

The formula 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 prohibitive due to infinite battery weight requirements. The battery shall have enough energy to propel at least itself on marketable distance. This is exactly the case with all existing batteries or the ones under development. They would not be able to drive itself, without wheels, frame, driver, etc., on a 200 mile distance at 55 mph.

In case of our batteries, at least the propulsion could take place. The battery weights are given in Table 13.

TABLE 13
PROPOSED BATTERIES WEIGHTS, LBS.

BATTERY	E _B Wh/kg	MID-SIZE CAR		COMPACT		SUB-COMPACT	
		W _R	W _{B+W_C}	W _R	W _{B+W_C}	W _R	W _{B+W_C}
Al-Fe-O	450	1,050	5,050	600	4,000	770	3,270
Al-Cu-O	440	1,100	5,100	820	4,000	800	3,300
Al-Fe-OH	380	1,300	5,300	1,000	4,200	900	3,500

They will add from 20 to 45% to the weight of the car, but they will be able to perform the function. There could be no subcompact electric car as it follows from the data in Table 13, moreover, the smaller the car, the larger percentage of its weight shall be allocated to the battery. And, finally, let's estimate the economics of our batteries. For comparison, what is the cost of electric energy to drive 200 miles at 55mph in a so-called mid-size car with the battery? The energy necessary to drive 4,000 lbs. is 120 kWh, see Table 11. The best Al-Fe-O battery adds an additional 1,050 lbs., so the total energy requirements will be ~150 kWh. The efficiency of charging could be assumed at 85%, then the charging energy shall be equal to ~180kWh. At current cost of electricity 6¢/kWh, we are going to pay \$10.80.

Now, what could be the additional cost of automobile imposed by the battery addition? Because of our permanent drive toward utilization of the most economical materials, now we can enjoy the cost benefits. In the best battery, Al-Fe-O, the largest percentage of payable weight belongs to iron. Assuming the same usage of electrode materials, we can conclude, that the cost of electrodes is ~32¢/lb in comparison with ~25¢/lb for pure iron. Further, if we are to admit that the complexity of the battery technology will be similar to the automobile technology, then the cost of the battery unit of weight will be 28% up the cost of the car per unit of weight, as it is made mainly from iron. For example, an existing mid-size car sale price is \$12,000 per 3,500 lbs. or \$3.43/lb. Then the addition of 1,050 lbs. of batteries will add \$4,600. This is a very optimistic estimate because the cost of existing batteries is \$50/kWh. In our case, the total energy capacity is 180/0.7 ≈ 260 kWh and the battery would cost ~\$13,000.

ALTERNATIVES FOR PROPULSION

Earlier in the paper we found practically the most economical solution for purely electric propulsion, from energy storage standpoint. Now let's compare that solution with two other alternatives. The first one, currently in use, is based on hydrocarbon fuels like gasoline. Those fuels are called non-renewable as the cost of their manufacturing from basic elements outweighs the cost of depletion of natural deposits. The second one, currently available, is based on alcohols like methanol and ethanol. They are also hydrocarbons, but are considered renewable in accordance with capabilities of existing agricultural technology, especially in our country. Table 14 concentrates data necessary to calculate the projected yearly cost of different fuels. The average mileage was estimated at

10,000 miles equivalent, from energy consumption on a system study level, to miles driven at 55 mph. This estimate is close enough to actual usage.

TABLE 14
YEARLY FUEL COST

CHARACTERISTIC	GASOLINE	Al-Fe-O	
		ETHANOL	BATTERY
Car weight with load, lbs.	4,000	4,000	4,000
Energy requirements for 200 miles @ 55mph, kWh	100	100	100
Efficiency of energy usage	30%	30%	85%
Energy content, kWh	333	333	120
Energy density, kWh/lb.	5.6	3.5	0.2 X 0.7
Fuel weight, lbs.	59	95	850
Fuel weight for its own propulsion, lbs.	1	2	200
Total fuel weight, lbs.	60	97	1,050
Fuel economy	21 mpg	14 mpg	--
Unit fuel cost, \$ for 200 mi at 55 mph	11.50	27.40	10.80 (electricity)
Yearly mileage	10,000	10,000	10,000
Yearly fuel cost, \$	575	1,370	540

Now let's analyze the results. The first striking discovery is that the current gasoline cost and electric energy cost are almost the same. It means that an electric car with add-on cost of batteries principally can't compete with gasoline cars now. Let's calculate at what increase in gasoline prices without any increases in electric energy cost the yearly payback could be achieved by switching to the most economical electric car. The difference in fuel costs shall be covered by the battery cost: Gasoline cost = \$4,600 + \$540 = \$5,140; and then the increase in price of gasoline shall be \$5,140/575 = 9 times. Most likely this would not happen in the next 20-25 years. So, the electric car is not a viable alternative to the gasoline-powered car for a long time.

Looking in the future for so-called renewable fuels like ethanol, we can be more assured in price stability. This fuel costs more than gasoline now but the trend to its use is vivid. The simple payback period for the owner of the electric car, in comparison with the ethanol car, will be \$4,000/(1,370 - 540) ≈ 5.5 years. It means that for a foreseeable future, the economy of ethanol production far outperforms the economies of battery production and electric energy production. Let's look deeper in the essence of a difference between ethanol and Al-Fe-O battery as energy storage means.

The battery recovery cycle consists of transformation of iron oxide to aluminum oxide during energy release and vice versa during energy intake. No external matters are used or released.

The ethanol recovery cycle includes environment. During energy release, ethanol burns with oxygen of the atmosphere thereby using natural abundance of oxygen. The products of reaction, CO₂ and H₂O, are then converted back to ethanol during two processes: one is photosynthesis in plants with sun energy intake and another one is special extraction and purification in man-built plants.

The efficiency of battery energy usage runs as high as 85% due to constant temperature process without significant change in entropy.

The efficiency of ethanol energy usage runs as low as 30% in accordance with Otto cycle thermodynamic efficiency at limited combustion temperatures.

But the battery energy is usable only on 70% due to limitation of durability, moreover, practical usage of battery materials runs at 20% in comparison with theoretical limit. So, the overall battery energy

usage is $0.85 \times 0.7 \times 0.2 \approx 0.12$ or 12%, which is very unfavorable in comparison with 30% in case of combustion. In addition to it, hydrocarbons, and ethanol as one of them, consist from lighter elements, carbon and hydrogen, than battery metals Al and Fe. We also don't need to carry oxygen for combustion while we have to have it in the battery. The bond energy difference of the combustion reactants is similar to the one we selected for the battery, so the theoretical difference in energy density between ethanol and our battery is mainly in atomic weight difference. The resulting effect is 3.5 kWh/lb in ethanol and 1.0 kWh/lb in the Al-Fe-O battery. This ratio is also 3.5 times in favor of ethanol. The combined difference in weights of ethanol and the battery, including additional battery weight for its own propulsion on 200 miles is:

$$\frac{3.5 \text{ kWh/lb}}{1.0 \text{ kWh/lb}} \times \frac{30\%}{12\%} \times \frac{1,050}{850} \approx \frac{1,050}{97} \approx 11.$$

One more important conclusion can be derived from a comparison of combustible fuels and electric energy source. Because the latter is greatly uneconomical, the blending of both those sources in one vehicle will inadvertently result in poorer economics. This is exactly the case with the Hybrid Vehicles Program of DOE. In accordance with their definition, a hybrid vehicle is "a vehicle that is fueled from more than one external source of energy, one source being electricity. A majority of propulsion energy must be supplied by the external electric source." Just like that.

Fortunately the idea of a hybrid vehicle is the most promising one in a sense of better economics of automobiles, but not in the way of DOE. The meaning "hybrid" shall be applied not to energy but to power. There is tremendous potential to increase the efficiency of utilization of regular internal combustion engine in EPA driving cycle. Here a peak power source with low energy content like a small starter battery could help immensely to improve ICE average utilization efficiency from ~10% to 30%, thereby increasing EPA fuel economy in ~3 times. That starter battery, used for the car and not for the engine, shall be operated in the same way as it is now, and be charged from the engine. So the car will have only one source of energy - combustible fuel - but two sources of power, of the average power supplied by the heat engine and of the peak power supplied by the battery.

Our definition of a hybrid vehicle can be as follows: a vehicle with a heat engine supplying all the energy and average power and an additional power converter connected between the engine and the drive train, supplying peak power requirements by means of time compression of the portion of energy received from the engine. The electric battery can be used as accumulator for time compression action.

Further analysis of this type of a hybrid vehicle deserves a separate paper and can be found partially in reference materials including this author's patent application.

CONCLUSION

It has been shown that the best practical rechargeable battery might be built based on oxygen exchange between aluminum and iron or copper.

There is a possibility to build a battery operating at ambient temperatures with practical energy density of 200 Wh/kg and 1,000 Wh/kg theoretically. A comparison was made of those batteries with several of the most advanced ones under development. It was shown that none of the existing batteries operating at ambient temperatures could power any car on 200 miles at 55 mph, and that the suggested battery might do it while adding 20-45% to the total vehicle weight.

Finally, it was shown that even in this case the battery option would probably have 6 years payback period at best in comparison with alternative of ethanol, renewable fuel, combustion.

Of course, the battery alternative for propulsion is economically notwithstanding the gasoline combustion and will be such for a long time. Hybrid Vehicle Program, in the definition of DOE, can't provide an economical solution for automobile propulsion.

One possible application for newly proposed batteries could be load leveling by utilities where long payback is acceptable.

MAIN STUDY BASE

- 1 Handbook of Chemistry and Physics, 58th edition, CRC Press, Cleveland, 1977
- 2 Automotive Handbook, 18th edition, Bosch
- 3 G. S. Altshuller, Algorithm of Invention, 2nd edition, "Moscow's Worker," Moscow, 1973 (in Russian)
- 4 G. W. Vinal, Storage Batteries, 4th edition, John Wiley & Sons, 1980
- 5 T. Erdely-Gruz, Die Chemischen Quellen Der Energie, Akademiai Kiado, Budapest, 1971
- 6 L. E. Unnewehr, S. A. Nasar, Electric Vehicle Technology, John Wiley & Sons, 1982
- 7 C. L. Gray, F. von Hippel, The Fuel Economy of Light Vehicles, Scientific American, v. 244, May 1981
- 8 Electric and Hybrid Vehicles, Noyes Data Corp., Park Ridge, N. J. 1979
- 9 R. U. Ayres, R. P. McKenna, Alternatives to the Internal Combustion Engine, John Hopkins University, Baltimore, 1972
- 10 Automotive Fuel Economy, Part 2, SAE, 1979
- 11 P.M. Heldt, High-Speed Combustion Engines, 14th edition, NY A CK, N. Y., 1948
- 12 Ford Motor Co., The Automobile as an Energy Converter, Technology Review, 2, 1975
- 13 Numerous publications of DOE, Electric and Hybrid Vehicle Program
- 14 EPA Driving Schedule
- 15 Selected U. S. Patents in the battery technology field: 3,993,502; 4,086,393; 4,146,680; 4,149,953
- 16 Selected U. S. Patents in the vehicle hybrid technology: 3,566,717; 3,732,751; 3,791,473; 4,148,192 and author's patent application 06/282,961