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# ANALYSIS OF POWER AND ENERGY IN ELECTROCHEMICAL PORTABLE POWER SYSTEMS

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**Abstract**. *Electrochemical power generation is an incredibly diverse and sophisticated field, and several major academic and corporate concerns throughout the world are racing for the ultimate electrochemical power solution, with particular attention to the massive potential markets of electric or hybrid vehicles and personal communication devices like cellular telephones. The two principal foci of these efforts have been batteries and fuel cells. Batteries and fuel cells are electrochemical devices that convert chemical energy into electrical energy by electrochemical oxidation and reduction reactions, which occur at the electrodes. A very useful graphical technique for comparing various personal power devices is a Ragone plot. The diagram is a log-log plot, which allows a significant spectrum of gravimetric power density (kW/kg) and gravimetric energy densities (kWh/kg) to be plotted compactly. In this paper, the relationship between power and energy for batteries and fuel cell system was analyzed. The characteristic parameters of the systems are considered to be independent variables, which are functions of the power and energy of the system. Mathematical expressions were derived to construct a Ragone plot for batteries and fuel cells that describes the power-to-stored energy trade-off based on partial data given by companies that produce fuel cells and batteries.*

***Keywords***: *Electrochemical power, batteries, fuel cells, specific energy, specific power.*

## 1. Introduction

Batteries and fuel cells are electrochemical devices that convert chemical energy into electrical energy by electrochemical oxidation and reduction reactions, which occur at the electrodes. The basic physical structure of batteries and fuel cells is an electrolyte layer sandwiched by an anode (negative electrode) and cathode (positive electrode) on either side. In a cell, the reactions occur at the electrode surfaces. In generalized terms, the reaction at the electrodes and the overall reaction can be represented by, respectively (Linden and Reddy, 2001):

$$a\,\mathrm{A} + n\,e^{-} \;\Leftrightarrow\; c\,\mathrm{C} \quad \text{(oxidation)} \tag{1}$$

$$b\,\mathrm{B} - n\,e^{-} \;\Leftrightarrow\; d\,\mathrm{D} \quad \text{(reduction)} \tag{2}$$

$$a\,\mathrm{A} + b\,\mathrm{B} \;\Leftrightarrow\; c\,\mathrm{C} + d\,\mathrm{D} \quad \text{(overall reaction)} \tag{3}$$

The change in the standard free energy, $\Delta G^0$, (i.e. the maximum electric energy that can be delivered by the chemicals that are stored within or supplied to the electrodes in the cell) of the reaction (3) is expressed as (Linden and Reddy, 2001; Hirschenhofer et al, 1994):

$$\Delta G^0 = -n_e\, F\, E^0 \tag{4}$$

Where: F is the Faraday constant (96,487 C/mol), $E^0$ is the standard potential (V) at 0.101 MPa and 298 K and $n_e$ is the number of electrons participating in the reaction. When the conditions are other than the standard state (0.101 MPa and 298 K), the voltage $E_0$ of a cell is given by the Nernst equation (Delpierre and Sewell, 2002):

$$E_0 = E^0 - \frac{R\,T}{n_e\,F}\ln\left[\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right] \tag{5}$$

Where: $a_i$ is the activity of relevant species, R is the gas constant and T is the absolute temperature. In the case of a fuel cell, the maximum work available from a fuel source is also related to the free energy of reaction ($\Delta G_R$), whereas the enthalpy of reaction ($\Delta H_R$) is the pertinent quantity for a heat engine (EG&G Technical Services, 2002):

$$\Delta G_R = \Delta H_R - T\Delta S_R \tag{6}$$

As shown in Eq. (6), the difference between $\Delta G_R$ and $\Delta H_R$ is proportional to temperature and to the change in entropy ($\Delta S_R$).

Electrode reactions are characterized by both chemical and electrical changes and are heterogeneous in type. They may be as simple as the reduction of a metal or the overall process may be relatively complex, involving several steps. Before the electron transfer step, electroactive species must be transported to the electrode surface by migration or diffusion. The electroactive species needs to be adsorbed by the electroactive material either before the electron step or after it. These behaviors lead to losses and prevent some chemical energy from being converted to useful electric work during cell discharge. To determine actual cell performance, three losses must be subtracted from the Nernst potential: (1) activation polarization, (2) concentration polarization, and (3) Ohmic polarization. When connected to an external load ($R$), the cell voltage V can be expressed as (Linden and Reddy, 2001):

$$V = E_0 - i\left(\eta_{\mathrm{act}} + \eta_{\mathrm{conc}} + R_i\right) = E_0 - i\,R_t \tag{7}$$

Where $\eta_{act}$ and $\eta_{conc}$ is the impedance due to activation and concentration losses, respectively; $R_i$ is the internal resistance of the cell and $i$ is the operating current. The Nernst equation characterizes the ability of the reactants to diffuse in the electrolyte from the bulk fluid flow and limits the current generation in the device. The activation polarization characterizes the energy needed to start the reaction. Activation losses are a function of the charge transfer kinetics of the electrochemical processes and are predominant at small current density. On the other hand, concentration polarization adjusts for the diffusion gradient into the active sites and is dominant when the cell is operating at high current density. Ohmic polarization is directly related to the internal resistance of the cell. It follows Ohm's law and describes the thermal losses caused by resistive heating that occur when a current passes through an electrolyte and through electrodes.

The operating temperature of the electrochemical devices is very important for both the electrochemical and thermal performance. Although the Nernst equation shows that the open circuit voltage decreases with increasing temperature, the performance at typical operating current densities increases with increasing temperature due to reduced mass transfer polarizations and Ohmic losses. Some fuel cells are designed to work at higher temperatures in order to enhance ion mobility. However, high temperatures can cause chemical deterioration of some devices by enhancing secondary reactions in the electrodes and electrolytes, which may result in a permanent capacity loss. The operating temperature also affects the thermal performance and safety of the electrochemical devices through the sensible heat (heat generated due to the mass of the cell), resistive heating, and heat transfer to the ambient. Information on the basic fundamentals of batteries (Linden and Reddy, 2001) and fuel cell systems (EG&G Technical Services, 2002; Hirschenhofer et al, 1994; Hoogers, 2002) can be found in the literature.

## 2. Fuel cells

A fuel cell generates electricity directly through electrochemical reactions. Fuel is transformed at the anode, and oxygen is transformed at the cathode. The transformations release electrons that are available to drive a load, and ions that are preferentially transported through an electrolyte. Figure 1 shows basic concepts of the main fuel cells used in portable power systems.

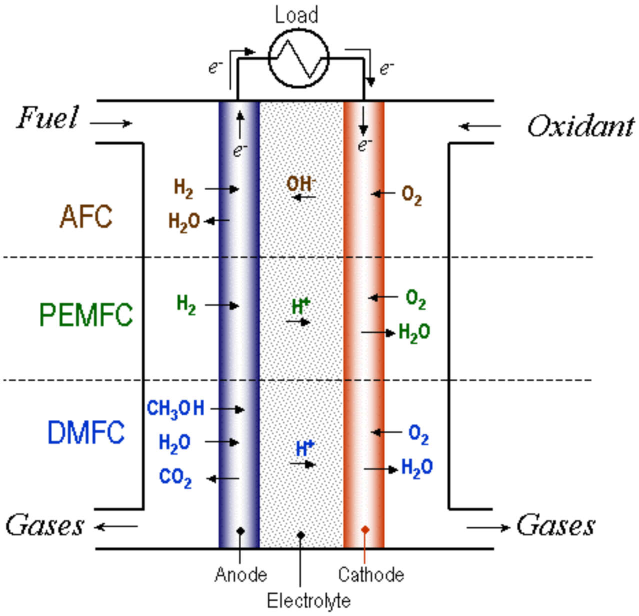

Figure 1. Basic concepts of an AFC, PEM and DM fuel cell (EG&G Technical Services, 2002).

Assuming that the weight of the fuel cell is a function of the power (P) delivered to the load, it follows (Kinoshita and Landgrebe, 1993):

$$W_{ws} = P\, f_{FC} / i\, V \tag{8}$$

Where $f_{FC}$ is a weight factor for the fuel cell device (weight/electrode area). This factor can be related to the weight and total area of the electrodes in the stack. Similarly, assuming the weight of the reactant subsystem ($W_{RS}$) is a function of the energy (E) delivered by the device (Kinoshita and Landgrebe, 1993):

$$W_{RS} = E\, f_{RS} / \mu\, F\, V \tag{9}$$

Where $F$ is Faraday's constant (26.8 Ah/eq), $\mu$ is energy conversion efficiency, and $f_{RS}$ is a factor that is a function of the amount of reactants (number of equivalents) and the weight of the auxiliary components (weight/equivalent of stored energy).

For a fuel cell, the gravimetric energy density (ED) is a measure of the total energy available in the device per unit mass and it is determined by the voltage of the cell and the amount of charge that can be stored in the fuel. Typical units for gravimetric energy density are Wh/kg and it can be calculated by (Pell and Conway, 1996):

$$ED = \frac{E}{W_{RS}} = \frac{\mu\, F\, V}{f_{RS}} \quad \text{or} \quad V = \frac{ED\, f_{RS}}{\mu\, F} \tag{10}$$

Gravimetric power density (PD) is the total power available in the device per unit mass (W/kg). It is related to the gravimetric energy density (PD = ED/t) at a given discharge rate, and indicates how rapidly the cell can be discharged and how much power can be generated. It can be given by (Pell and Conway, 1996):

$$PD = \frac{P}{W_{FC}} = \frac{i\, V}{f_{FC}} \tag{11}$$

Substituting Eq. (7) and (10) in Eq. (11) yields:

$$PD = \frac{[E_0 - V]\, V}{R_t\, f_{FC}} = \frac{ED\, f_{RS}}{\mu F\, R_t\, f_{FC}} \left[ E_0 - \frac{ED\, f_{RS}}{\mu F} \right] = \frac{E_0^2}{R_t\, f_{FC}} \left[ \frac{ED\, f_{RS}}{\mu F\, E_0} - \left( \frac{ED\, f_{RS}}{\mu F\, E_0} \right)^2 \right] \tag{12}$$

Defining $q_0 = \mu F$ as the maximum available capacity of the reactant (when $\mu = 1$), the maximum electrical energy that can be obtained by electrochemical conversion of the reactant is $q_0 E_0$. Substituting this in Eq. (12) gives:

$$PD = \frac{E_0^2}{R_t\, f_{FC}} \left[ \frac{ED\, f_{RS}}{q_0\, E_0} - \left( \frac{ED\, f_{RS}}{q_0\, E_0} \right)^2 \right] \tag{13}$$

## 3. Batteries

In addition to fuel cell-based electrochemical power, an intense research and development effort is currently underway in batteries. The principal focus is lithium batteries. In their simplest form, batteries consist of two dissimilar electrode materials (positive electrode or cathode and negative electrode or anode) that are separated by an ionic conductor, which may be liquid, polymer, or solid phase. The characteristic performance of a battery is dictated by the type of electrode material and electrolyte (ionic phase that is usually held in a porous matrix that is often referred to as the separator). Because the electrolyte must be compatible chemically and electrochemically with the electrode materials, the combination of electrolytes and electrodes are limited. For example, commercial lithium-manganese dioxide batteries must use non-aqueous electrolytes because Li reacts rapidly with water.

Batteries are generally first classified as primary or secondary. The primary battery cannot be recharged electrically after discharge. A secondary battery can be recharged electrically, after discharge, by passing current through it in the opposite direction to that of the discharge current. This kind of battery is generally characterized by relatively high gravimetric power density, high discharge rate, flat discharge curves, and good low temperature performance.

Lithium-ion batteries have specific energies of around 160 Wh/kg and are expected to show substantial near- and mid-term increases in capacity, rate capability, and stability. Discontinuous improvements in performance are expected to result from the introduction of new materials, including positive electrode materials. Service life is also expected to improve substantially as one proceeds to smaller and smaller particle sizes making up the active materials within the interface regions.

According to McLarnon *et al.* (1988) the energy density-power density relationship for batteries is:

$$\mathrm{PD} = \frac{\mathrm{E}_0^2}{R_t}\left[\left(\frac{\mathrm{ED}}{q_0\ \mathrm{E}_0}\right)^{0.5} - \frac{\mathrm{ED}}{q_0\ \mathrm{E}_0}\right] \tag{14}$$

It is interesting to note that the form of Eq. (14) is similar to that for Eq. (13), differing in the exponents and in the inclusion of the factors $f_{\mathrm{FC}}$ and $f_{\mathrm{RS}}$, which are related to the characteristics of the fuel cell stack and the reactant subsystem.

The most common properties or characteristics used for the selection of a battery system are specific energy, capacity, operating voltage, operating temperature, service life, cycle life (for secondary batteries), shelf life, self discharge rate, safety and reliability, and cost. As a first approximation, the practical specific energy obtained in a battery is about 20% to 25% of the theoretical specific energy calculated for the battery reaction. The theoretical voltages and capacities of some electrochemical systems used in personal power systems are given in Table 1. The most advantageous combinations of anode and cathode materials are those that will be lightest while giving a high cell voltage and capacity. Figure 2 is an approximate Ragone plot of several battery chemistries.

Table 1. Voltage, capacity and specific energy of some battery systems [Linden, Reddy, 2001].

| *Battery type* | *Anode* | *Cathode* | *Theoretical gravimetric energy density [Wh/kg]* | *Practical gravimetric energy density [Wh/kg]* | *Fraction [%]* |
|---|---|---|---|---|---|
| Lead-acid | Pb | $PbO_2$ | 252 | 30 – 50 | 12–20 |
| Ni-Cd | Cd | Ni oxide | 244 | 45 – 80 | 18–33 |
| NiMH | MH * | Ni oxide | 240 | 60 – 120 | 25–50 |
| Li-ion | $Li_xC_6$ | $Li_{(1-x)}CoO_2$ | 410 | 110 – 160 | 27–40 |
| Li-polymer | $Li_xC_6$ | $Li_{(1-x)}CoO_2$ | 410 | 100 – 130 | 24–32 |

* MH = metal hydride, data based on 1.7% weight of hydrogen storage.

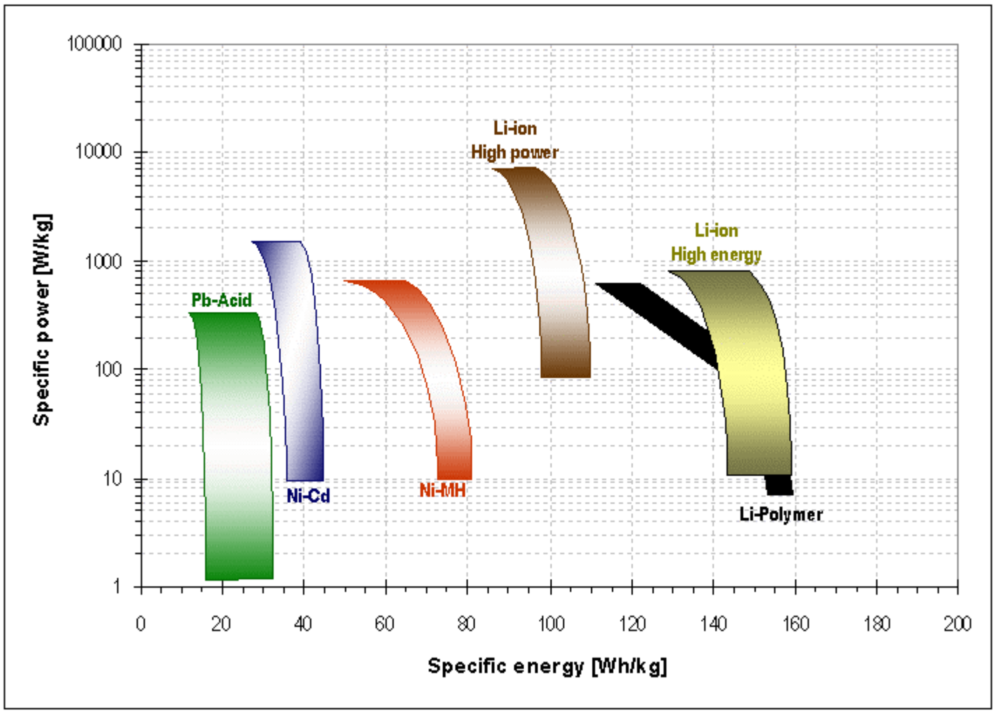

Figure 2. Ragone plot of some battery systems [Mcdowall, 2004].

## 4. Results and discussion

Table 2 shows the specifications for proton exchange membrane fuel cell (PEMFC) systems commercially, or to be commercially, available, Table 3 shows the specifications of direct methanol fuel cell (DMFC) and magnesium-air fuel cells, and Table 4 shows the specifications for commercial lithium batteries. The calculations for fuel cells and batteries used the equations shown above in this paper and all of the specifications in Tables 2 to 4. Figures 3 to 5 show the theoretical Ragone plots for the systems displayed in Tables 2 to 4. The results show that Li-ion batteries have the highest gravimetric power density while magnesium-air fuel cells and direct methanol fuel cells have the highest gravimetric energy density. These behaviors are expected since fuel cells are still in development and their performance depends heavily on the reactant subsystem weight.

Table 2. Specifications for PEMFC systems commercially (or to be) available.

| **Company** | **Product** | **Power [W]** | **Volume (L)** | **Weight FC (kg)** | **Weight RS (kg)** |
|---|---|---|---|---|---|
| ReliOn | Independence 1000 | 1000 | 157 | 69 | 40 |
| Ball Aerospace & Technology Corp. | PPS 50 | 50 | 4.3 | 2.95 | 2.3 |
| Ball Aerospace & Technology Corp. | PPS 100 | 100 | 5.6 | 3.86 | 4.6 |
| Ballard Power Systems, Inc. | AirGen | 1000 | 132.5 | 49 | 60 |
| H Power Corp. | PowerPEM D35 | 35 | 5.1 | 1.2 | 2.3 |
| H Power Corp. | PowerPEM SSG50 | 50 | 12.5 | 1.8 | 3.2 |
| Hydrogenics Corp. | HyPORT C | 500 | 71.4 | 25 | 10 |
| Voller Energy Ltd | Portapack VE 100 | 100 | 17.4 | 10 | 1.65 |
| Voller Energy Ltd | Portapack VE 1000 | 1000 | 150 | 18 | 60 |

FC: fuel cell; RS: reactant subsystem.

Table 3. Specifications for other FC systems commercially (or to be) available.

| **Company** | **Product** | **Power [W]** | **Volume (L)** | **Weight FC (kg)** | **Weight RS (kg)** |
|---|---|---|---|---|---|
| Ball Aerospace & Technology Corp. | PPS 20 (DMFC) | 20 | 1.3 | 1.0 | 0.4 |
| IdaTech Company | FCS 1200 (DMFC) | 850 | 326.8 | 60 | 24 |
| Smart Fuel Cell | SFC A25 (DMFC) | 25 | 21.9 | 7 | 2.70 |
| Toshiba | (DMFC) | 12 | 0.8 | 0.8 | 0.22 |
| Greenvolt Power Corp. | PM-122 (Magnesium) | 100 | N/A | 2.4 | 1.0 |
| Greenvolt Power Corp. | PM-340 (Magnesium) | 340 | N/A | 5.6 | 2.1 |

FC: fuel cell; RS: reactant subsystem.

Table 4. Specifications for commercial Li-ion batteries.

| **Company** | **Weight (kg)** | **Mid-discharge voltage $^1$ (V)** | **Discharge capacity at *C*/5 (Ah)** | **Polarization resistance $^2$ ($\Omega$ cm$^2$)** |
|---|---|---|---|---|
| Sony | 0.60 | 3.50 | 1.18 | 213 |
| NEC Moli | 0.48 | 3.75 | 1.30 | 189 |
| A & T | 0.50 | 3.75 | 1.45 | 54 |
| Sanyo | 0.45 | 3.75 | 1.30 | 118 |
| Matsushita | 0.40 | 3.75 | 0.82 | 50 |

1: Theoretical voltage of 4.2 V; 2: at rates above 1*C*.

Tables 2 and 3 show data collected from manufacturers of the systems. The weight of the reactant subsystem was either given by the manufacture's data sheet or derived by the assumption of the use of a K-cylinder of hydrogen (60 kg). Table 4 presents some physical characteristics, cycling conditions of the cells and the performance characteristics of the electrodes and the cells. The data were collected from the manufactures of the batteries.

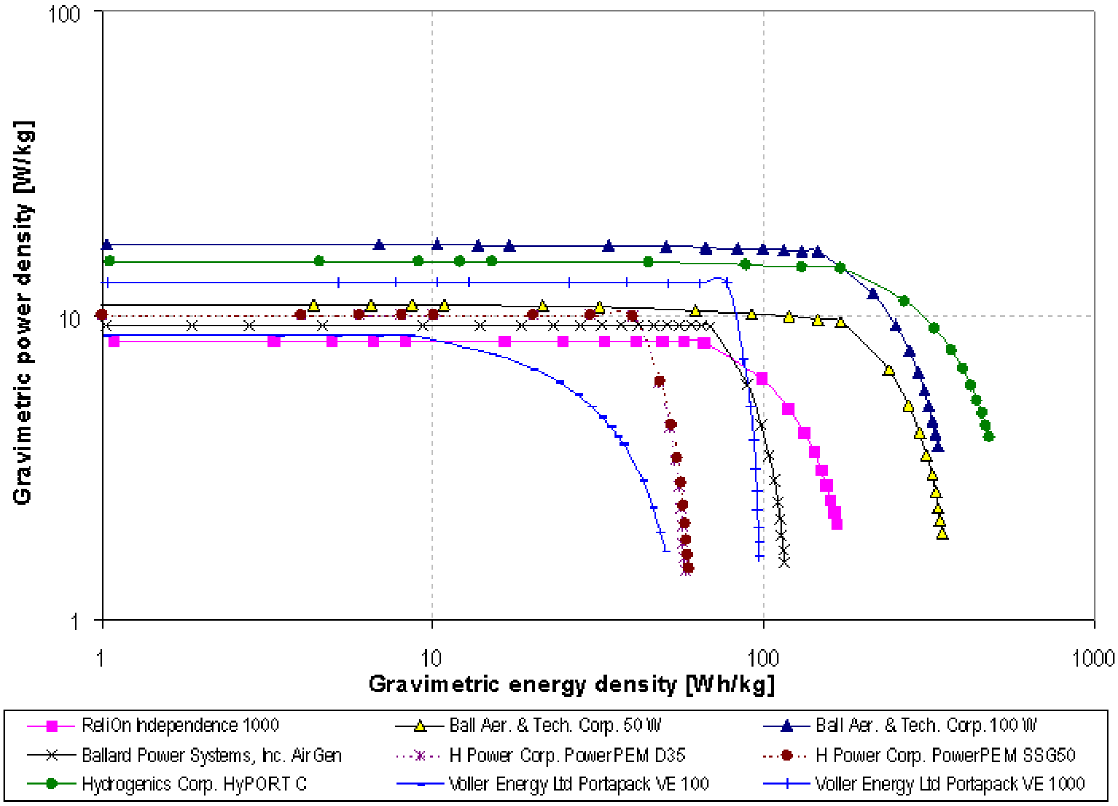

Figure 3. Predicted Ragone plots for PEMFC systems.

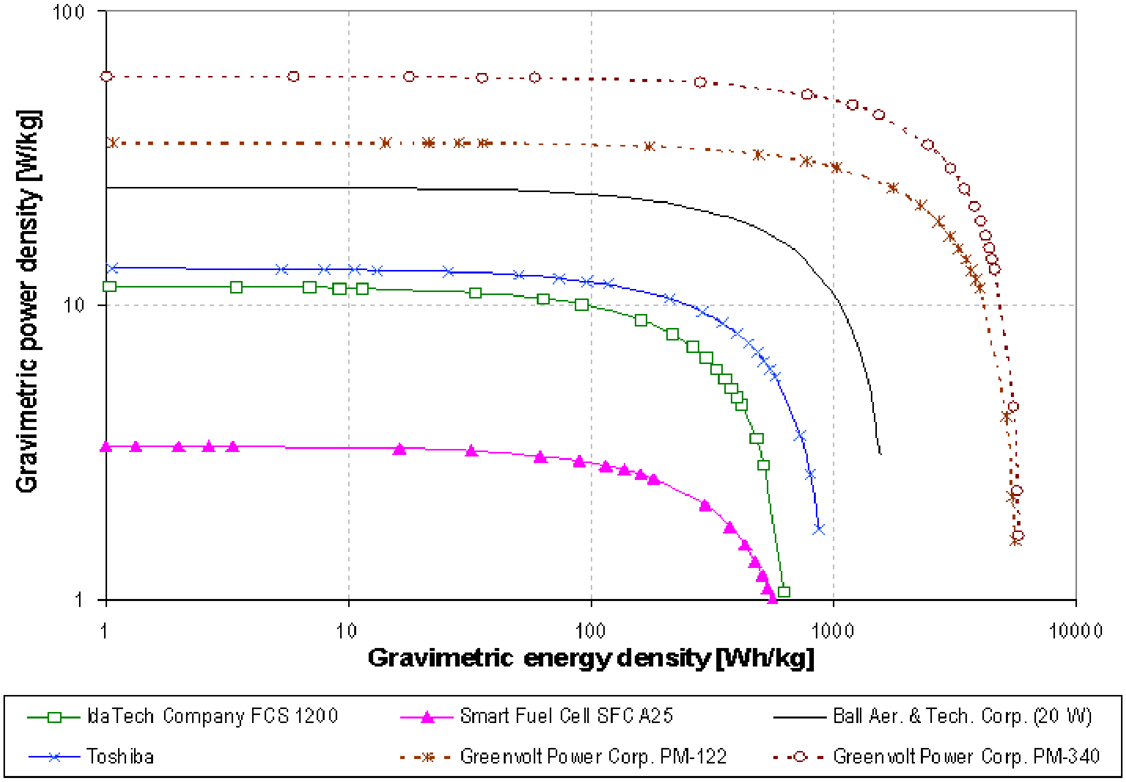

Figure 4. Predicted Ragone plots for the fuel cell systems listed in Table 3.

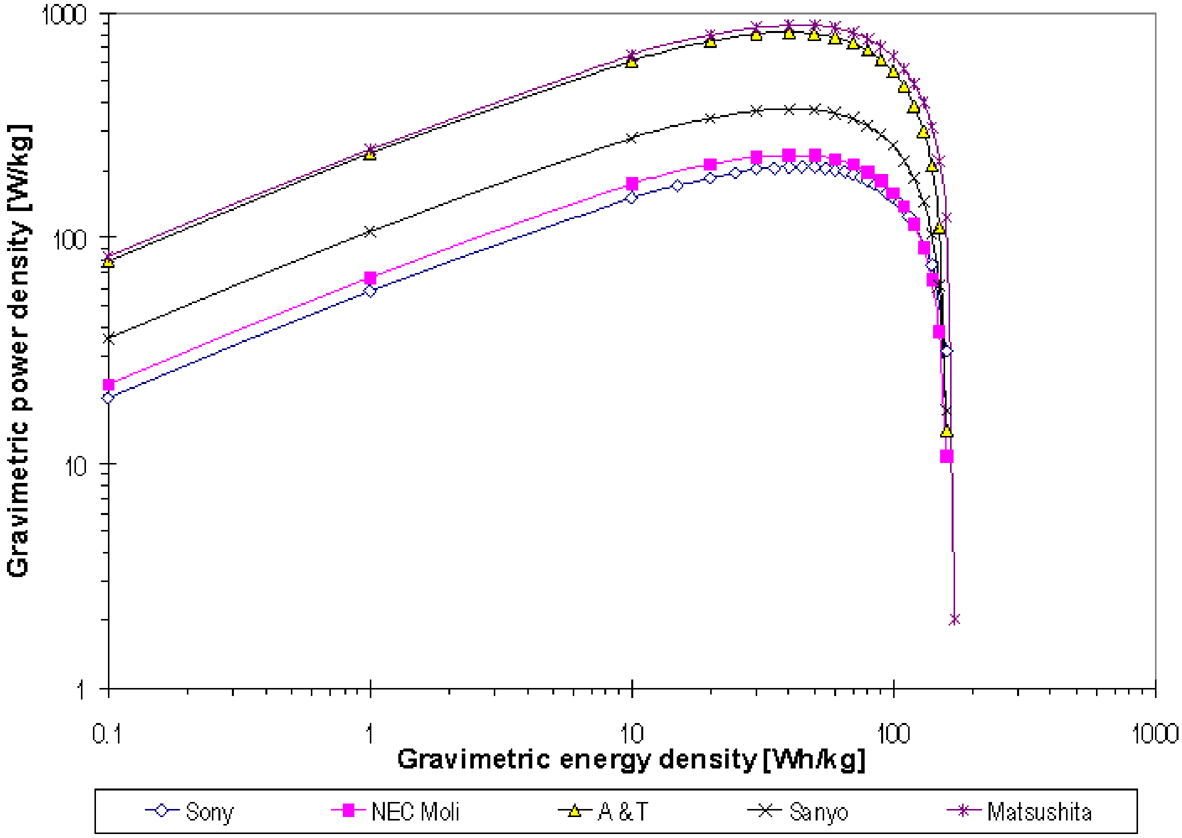

Figure 5. Predicted Ragone plots for battery systems listed in Table 4.

A simple comparison of Figures 3 to 5 indicates that Li-ion batteries continue to outperform fuel cells in terms of gravimetric power density. PEMFC, in particular, have relatively weak gravimetric performance because they cannot utilize the most energy dense fuels easily or efficiently. The highest performing fuel cells use solid fuels, acting essentially as batteries with replaceable fuel tanks. Despite their limits in terms of power density, fuel cells can provide substantial improvements in gravimetric energy density performance over batteries. Because, unlike with batteries, the fuel tank weight in a fuel cell can be independent of the stack weight, the ultimate energy density is essentially the fuel's energy density times the efficiency of the fuel cell (which can be quite substantial). Hence, despite the limitations in gravimetric power density, fuel cells can be a good portable power choice when the application requires long operating duration between recharge or refueling.

Although fuel cells were first explored as portable power units in the 1960s, widespread interest in portable fuel cells is a relatively recent phenomenon, with significant research efforts by the major companies often being less than five years old. In such a recently developed market, it is dangerous to expect quick introduction of fuel cell products. Perhaps the most encouraging sign of a successful fuel cell future is that the driving force behind developments in this sector is the end user. Major electronics manufacturers want greater gravimetric power density and energy for their consumer products, while the military is looking to increase its capabilities using new technology; and both view fuel cells as a possible solution. As a result, the portable fuel cell industry looks in a healthy state. The true test is still to come, as to whether fuel cell technology can compete in all the sectors currently being investigated. However, more and more prototypes and early series products are being designed and manufactured by an ever-growing number of companies. At the moment, the future looks reasonably bright for some contribution by fuel cells in the personal power realm.

## 5. Conclusion

As technology advances, the power requirements of personal power systems also change. Electrochemical power systems have to meet some requirements such as high gravimetric energy density and gravimetric power density (performance), light weight, and low cost.

The goal for batteries continues to be higher power with no increase in size, weight or cost. Nickel-metal hydride (NiMH) batteries are currently the standard battery used in hybrid electric vehicles; they offer a gravimetric energy density of about 50 Wh/kg and gravimetric power density up to 1,100 W/kg. The technology is relatively mature, though modest near- to medium-term increases in discharge rate capability are likely, mainly through improvements in engineering design rather than new materials or nanostructures (Han et al., 2003). Li-ion batteries have specific energies of around 160 W/kg and are expected to show more substantial near- and mid-term increases in capacity, rate capability, and stability. Discontinuous improvements in performance are expected to result from the introduction of new materials, including positive electrode materials. Service life is also expected to improve substantially as one proceeds to smaller and smaller particle sizes making up the active materials within the interface regions

Fuel cells are assessed relative to the battery technologies they are expected to replace, specifically Li-on and Li-polymer. Since pricing is a critical factor in whether fuel cells can displace current battery technologies or wall-plug chargers, much depends on finding new materials and on developing low cost manufacturing strategies. These have been the historical challenges to fuel cells since their discovery and demonstration. Further research in this area is justified however it is not the subject of the presented paper.

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