
Electrochemical Power Sources

2. Fuel Cells and Supercapacitors

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Part 1. A K Shukla and S K Martha, Rechargeable Batteries, *Resonance*, Vol.6, No.7, p.52, 2001.

Motor-vehicle industry is presently pursuing technologies capable of eliminating emissions with higher fuel-efficiencies. Fuel cells and more recently, electrochemical supercapacitors have been found to be attractive options for electric vehicles. Fuel cells convert the chemical energy of a fuel directly into dc electricity with fuel efficiencies higher than the conventional internal-combustion engines. Supercapacitors store electrochemical energy reversibly much akin to rechargeable batteries. Although, supercapacitors have limited energy densities, they can provide higher power densities than those achievable with rechargeable batteries. This article provides a brief description of the six generic types of fuel cells and the supercapacitors.

Fuel Cells

Like rechargeable batteries, fuel cells deliver energy by consuming electroactive chemicals but differ significantly in that these chemicals are delivered on-demand to the cell. Typically, these chemicals consist of a hydrogen-rich fuel supplied to the anode and air to the cathode. As a result, a fuel cell can generate energy continuously and for as long as the electroactive chemicals are provided to the cell. Thus, fuel cells have the potential to solve the most challenging problem associated with the currently available battery systems, namely their insufficient energy at a given weight or volume. Besides, while the leading battery technologies are reaching the practical limits of their energy storage capabilities, commercial fuel cell technology is still in its infancy.

The basic cathode-electrolyte-anode construction for a fuel cell



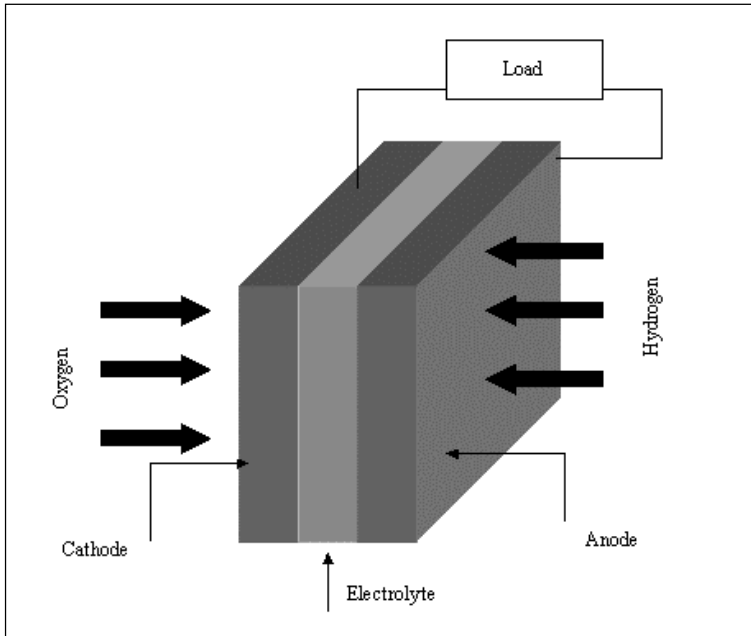


Figure 1. Basic cathode-electrolyte-anode construction of a fuel cell.

is shown schematically in *Figure 1*. Although, the first hydrogen-oxygen fuel cell was demonstrated as early as in 1839 by Sir William Grove, the surfeit of rich development in fuel cell technology has come about practically during the last 50 years, initially with developments for the space industry in the sixties followed by the demand during the energy crisis of the seventies and more recently with the push to electric cars. Since hydrogen does not occur naturally as a gaseous fuel, it has to be generated from a locally available fuel source, such as natural gas, gasoline or methanol. A small local store of hydrogen is also essential in the use of fuel cells for portable applications. Although hydrogen can be stored as a compressed gas or a liquid, chemical methods can also be used. There are many compounds, such as metal hydrides, which can hold quite large quantities of hydrogen in relation to their mass. For terrestrial applications, oxygen supply to the fuel cell systems is usually met from air.

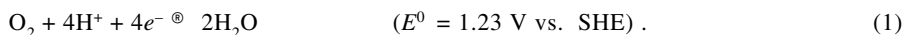
Although several fuel cell concepts have been tested in the laboratory, the systems that are being potentially considered for commercial development are: (i) Phosphoric acid fuel cells

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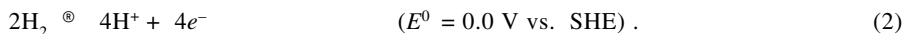


Box 1. Electrochemistry of the Phosphoric Acid Fuel Cells (PAFCs)

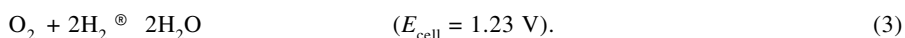
At the cathode:



At the anode:



Accordingly, the net cell reaction in the PAFC is given as:



(PAFCs) (ii) Alkaline fuel cells (AFCs) (iii) Molten carbonate fuel cells (MCFCs) (iv) Solid oxide fuel cells (SOFCs) (v) Polymer electrolyte fuel cells (PEFCs) and (vi) Solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs).

(i) Phosphoric Acid Fuel Cells (PAFCs): Phosphoric acid fuel cells for terrestrial applications have shown promise for commercialization. PAFCs operate at $\sim 200^\circ\text{C}$ with ion conduction through electrolyte being provided by protons. Platinum and platinum-metal alloys are employed in PAFCs as electrocatalysts with carbon-based electrodes. At such high temperatures, the problems of the stability of the carbon as also the catalysts arise. The advantages of PAFCs are that the phosphoric acid is very stable and can be highly concentrated ($\sim 100\%$) such that the water vapor pressure is low and hence keeping the steady-state water removal by the reactant gases equals the product water rate. Besides, at 200°C , the anode performance is good even with fuels containing carbon monoxide up to 5%. But, PAFCs suffer from slow kinetics for oxygen reduction reaction due to the strong adsorption effects of anions on to the active sites of the catalyst.

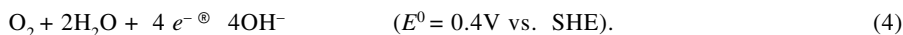
Platinum and platinum-metal alloys are employed in PAFCs as electrocatalysts with carbon-based electrodes.

(ii) Alkaline Fuel Cells (AFCs): Alkaline fuel cells are the most promising systems for space applications and have been used successfully in Apollo and other space missions. The advantages of AFCs are that they operate at room temperature, the cathode

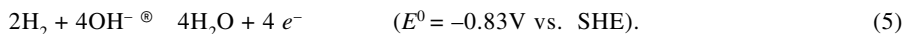


Box 2. Electrochemistry of the Alkaline Fuel Cells

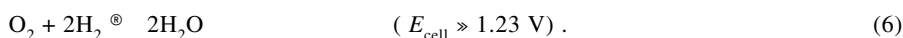
At the cathode:



At the anode:



Accordingly, the net cell reaction is:



performance is much superior and the construction materials are less costly than PAFCs. But the alkaline electrolytes react with carbon dioxide to form carbonates which severely limits the cell performance necessitating its scrubbing in the system. Owing to this drawback, presently AFCs are not being considered for terrestrial applications.

(iii) Molten Carbonate Fuel Cells (MCFCs): Molten carbonate fuel cells have several advantages over PAFCs. They have higher power density and higher cell voltages than PAFCs. The electrolyte employed is generally a mixture of alkali metal carbonates and the ion conduction is through the carbonate ions. These salts function as electrolyte only in liquid phase and therefore the cell operates at 600-700 °C. Since the cell is tolerant to carbon monoxide, reforming processes can occur within the fuel cell, and hence reformers and shift converters are not required. Higher efficiencies are achieved since the reforming process absorbs heat, which is supplied *in situ* by the heat produced at the electrodes of the cell. However, at high temperatures several constraints arise on materials suitability for long-time operations. Furthermore, MCFCs present a more difficult problem in carbon dioxide removal than AFCs because about four-times more carbon dioxide per kW of power output has to be transferred in a MCFC plant in relation to an AFC plant.

(iv) Solid-Oxide Fuel Cells (SOFCs): Solid oxide fuel cells

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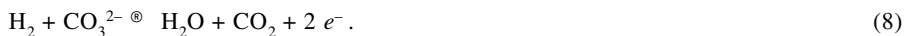


Box 3. Electrochemistry of the Molten Carbonate Fuel Cells

At the cathode:



At the anode:



Accordingly, the net cell reaction is given as:



employ solid, non-porous metal-oxide based electrolytes with ion conduction occurring through the migration of oxide-ions in the crystal lattice. Stabilized zirconia is commonly used as the electrolyte and the operating temperatures of the cells are between 900-1100 °C. In recent years, the discovery of the strontium- and magnesium-substituted lanthanum gallate perovskite and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolytes that have appreciable oxide-ion conductivity at ~600 °C has provided the possibility of develop-

Box 4. Electrochemistry of the Solid-Oxide Fuel Cells

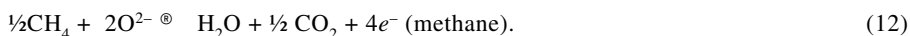
At the cathode:



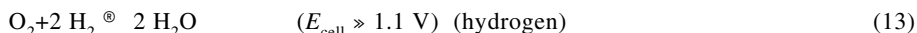
At the anode:



or,



Accordingly, the net cell reactions are given as:



or,



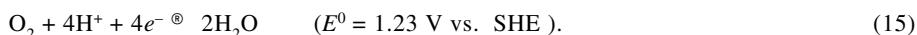
ing intermediate-temperature SOFCs operating between 600–700 °C. SOFCs have distinct advantages over aqueous electrolyte fuel cells as these employ no liquids and hence the problems associated with the flooding of porous electrodes and the maintenance of 3-phase interface are totally averted. Also, the electrolyte remains invariant and is independent of the compositions of the fuel and oxidant. Since the cell operates at high temperatures, losses due to activation polarization are minimized which avoids the use of noble metal catalysts. In addition, these fuel cells do not suffer from the constraints associated with MCFCs which require recycling of carbon dioxide at the cathode.

Polymer electrolytes have excellent oxygen solubility and diffusivity characteristics and are therefore expected to yield very good performance.

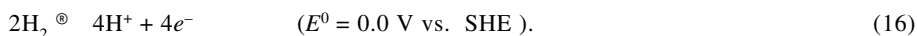
(v) Polymer-Electrolyte Fuel Cells (PEFCs): Polymer-electrolyte fuel cells employ an ion-exchange membrane, for example Nafion[®] – a hydrated perfluoro sulfonic acid, as electrolyte, which is impermeable to gases. PEFCs hold certain advantages over those with immobilized electrolytes as they provide a non-volatile electrolyte below 100 °C, a drastic reduction in corrosion, and materials related problems, negligible electrolyte leaching (as water is the only reaction product), and a thin electrolyte layer. Polymer electrolytes have excellent oxygen solubility and diffusivity characteristics and are therefore expected to yield better performance than any of the fuel cell systems discussed above. The main disadvantage is the necessity to humidify the electrolyte during its operation.

Box 5. Electrochemistry of the Polymer-Electrolyte Fuel Cells

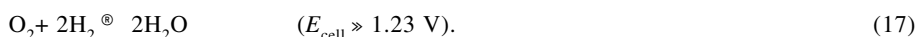
At the cathode:



At the anode:



Accordingly, the net cell reaction is given as:



Electrical System Efficiency (%)	PAFC 36-45	PEFC 32-40	MCFC 43-55	SOFC 43-55	AFC 26-31	DMFC ~ 40
Some Applications# Cogeneration	2	1	3	4	-	-
Utility Power	3	-	2	1	-	-
Distributed Power	3	4	2	1	-	-
Utility Repowering	3	-	2	1	-	-
Passenger Vehicles	-	3	-	-	1	2
Heavy Duty Vehicles	2	4	-	1	-	3
Portable Power	-	2	-	-	-	1
Speciality Power	-	3	-	-	1	2

#The degree of priority is 4 > 3>2>1.

Table 1. Efficiencies and envisaged applications of various fuel cell systems.

(vi) **Solid-Polymer Electrolyte Direct Methanol Fuel Cells (SPE-DMFCs):** SPE-DMFCs employ methanol directly as the fuel and hence eliminate the complexity of the reformer unit in the system. Since the methanol is fed with ample water, it also avoids complex humidification and thermal management problems associated with the PEFCs. Consequently, SPE-DMFCs provide advantage of lower system size as well as weight in relation to any of the existing fuel cell systems. But, SPE-DMFCs suffer from methanol cross-over problem across the Nafion membrane which affects the performance of the cathode and hence the cell during its operation. It is noteworthy that among the fuel cell systems discussed above, only PEFCs, AFCs and SPE-DMFCs are considered fit for electric cars (Table 1). At present, however, only PEFCs and SPE-DMFCs are being considered as serious contenders since, as indicated earlier, AFCs require pure CO₂-free hydrogen and oxygen (or air) to avoid carbonation of the electrolyte. As is seen from Table 1, SPE-DMFCs can provide a comparable efficiency in relation to PEFCs.

Electrochemical Supercapacitors

Electrochemical supercapacitors (ECs) or ultracapacitors are unique devices exhibiting 20-200 times larger capacitance than a conventional capacitor, which consists of two plates separated by a gas or vacuum as the dielectric. When a metal (or an electronic

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Box 6. Electrochemistry of the Solid-Polymer Electrolyte Direct Methanol Fuel Cells

At the cathode:



At the anode:



Accordingly, the net cell reaction is given as:



conductor) is brought in contact with a solid or liquid ionic-conductor, a charge accumulation is achieved electrostatically on either side of the interface leading to the development of an electrical double-layer, which is essentially a molecular dielectric. No charge transfer takes place across the interface and the current observed during this process is essentially a displacement current due to the rearrangement of the charges (conventionally described as an ideally-polarized electrode). Therefore, this process is non-faradaic¹ in nature. Besides, the charge storage is also achieved by an electron transfer that produces oxidation state changes in the electrostatic materials according to Faraday's laws in relation to electrode potentials (the so called ideally-reversible electrode). Thus, this process is faradaic² in nature. Accordingly, two types of supercapacitors have been developed and tested. One operates, by charging and discharging of the interfacial electrical-double-layer. In the second type, often called as pseudocapacitors or redox capacitors, the charge-discharge mechanism involves the transfer of electric charge between the phases but without any bulk-phase transformation. The electrons involved in the non-faradaic electrical-double-layer charging are the itinerant conduction-band electrons of the metal or carbon electrode while the electrons involved in the faradaic processes are transferred to or from valence-electron states (orbitals) of the redox cathode or anode reagent. The electrons may however arrive in or depart from the conduction-

¹ Non-Faradaic Process: In a non-faradic process charge accumulation is achieved electrostatically by positive and negative charges residing on two interfaces separated by a dielectric.

² Faradaic process: In a faradaic process, the charge storage is achieved by an electron transfer that produces chemical changes in electroactive materials according to Faraday's laws.



Suggested Reading

- [1] K Kordesch and G Simader, *Fuel Cells and their Applications*, VCH, Weinheim, 1996.
- [2] J Larminie and A Dicks, *Fuel Cell Systems*, Wiley, 2000.
- [3] B E Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer-Plenum Publishers, New York, 1999.
- [4] A K Shukla, S Sampath and K Vijayamohan, *Current Science*, Vol.79, p. 1656, 2000.
- [5] R C Bhardwaj and J Than, *J. Power Sources*, Vol. 91, p.51, 2000.

Gel electrolytes hold the promise of combining the advantage of solid-polymer electrolytes with the increased voltage of non-aqueous systems.

band states of the electronically-conducting support material depending on whether the fermi level in the electronically-conducting support lies below the highest occupied state (HOMO) of the reductant or above the lowest unoccupied states (LUMO) of the oxidant. In pseudocapacitors, the non-faradaic double-layer charging process is usually accompanied by a faradaic charge-transfer.

Accordingly, the capacitance (C) of a supercapacitor is given by,

$$C = C_{dl} + C_f \quad (21)$$

where C_{dl} is the electrical double-layer capacitance and C_f is its pseudocapacitance. The pseudocapacitance (C_f) is brought about by a surface redox-reaction of the type,



where O_{ad} and R_{ad} are the adsorbed oxidants and reductants, and n refers to the number of electrons (e).

In general, C_f (typically, $q_f = 220 \text{ mC cm}^{-2}$) \gg C_{dl} (typically, $q_{dl} = 20 \text{ mC cm}^{-2}$), where q_f and q_{dl} are charges associated with the pseudocapacitance and the electrical double-layer, respectively. It is estimated that the energy ($E = \frac{1}{2} CV^2$) stored in a one volt electrical-double-layer capacitor with porous carbon electrodes having a surface area of $1000 \text{ m}^2/\text{g}$ is $\sim 28 \text{ Wh/kg}$. By comparison, a one volt supercapacitor with a pseudocapacitance held between carbon electrodes of a similar surface area could store as large as $\sim 1876 \text{ Wh/kg}$ of energy. In practice, however it has not been possible to achieve these energy densities with any of the supercapacitors developed so far. But this suggests a definite scope for technology development in supercapacitors.

In recent years, phenomenal progress has been made in the development of ECs. At present, the development of non-aqueous systems appears to be gaining momentum due to the increased energy density of these systems. Gel electrolytes hold



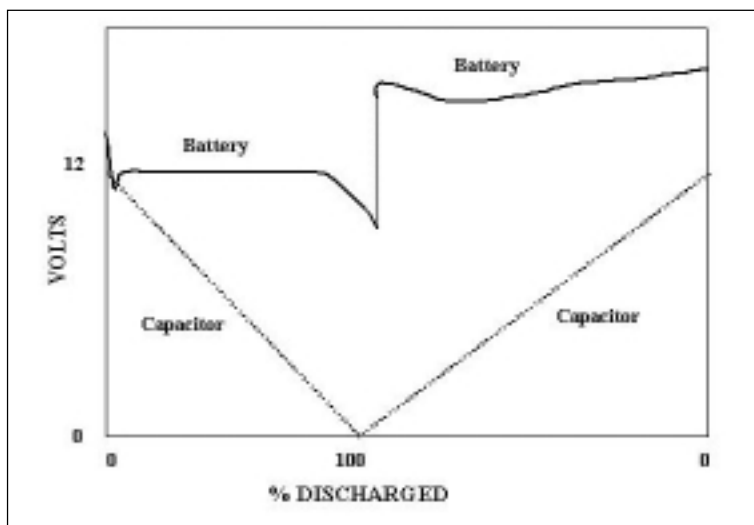


Figure 2. A comparison between charge-discharge characteristics of a battery and a supercapacitor.

the promise of combining the advantage of solid-polymer electrolytes with the increased voltage of non-aqueous systems. Nevertheless, only the carbon and the ruthenium oxide based supercapacitors have so far been commercialized while other systems are under various stages of development.

ECs have a number of advantages over rechargeable batteries. ECs can be both rapidly charged and discharged, and can deliver power densities in excess of 1 kW/kg albeit at relatively low energy densities typically less than 10 Wh/kg. The charge-discharge characteristics of a battery and supercapacitor are compared in *Figure 2*. Recently, lead-acid batteries with thin metal film (TMF[®]) technology have been developed which can deliver power densities as high as 6 kW/kg. ECs can be configured both in unipolar and bipolar configurations, require little maintenance, and are made from non-toxic and relatively inexpensive materials. With these characteristics, ECs appear ideally suited for meeting the burst acceleration power requirements of an electric car at relatively low-weight penalty.

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