Energy Storage and Retrieval

The Secondary Battery Route

A K Shukla and P Vishnu Kamath

Harnessing sunlight for the production of electrical energy is an engrossing prospect. The crucial concept underlying the success of solar power stations is energy storage and its retrieval on demand which can be most effectively achieved with storage batteries. This article highlights the chemistry of existing and emerging battery technologies.

Technological development in this century has been characterized not only by the increasing consumption of energy but also by the emergence of hydrocarbons as the primary source. The process of development is threatened by the limited reserves of coal and oil. In addition, the deleterious effects of excessive consumption of hydrocarbons on the economy and ecology of a large part of the world is too well known to be recounted here. These have brought into sharp focus the need for developing new environmentally benign *non-conventional* or what we would prefer to call *alternative energy sources*.

Wind, solar and tidal energies are available in almost all parts of the globe and the efficacious harvesting of these energy sources will also alleviate the problems associated with energy transmission and distribution. However these energy sources are intermittent and exhibit annual, seasonal as well as diurnal variations. They are available at certain times of the day or year and not available at other times. The key to the successful utilisation of these energy sources lies in the development of suitable energy storage devices.

Among the many energy storage devices presently in vogue, batteries are the most common. Batteries are electrochemical devices which convert chemical energy into electrical energy.

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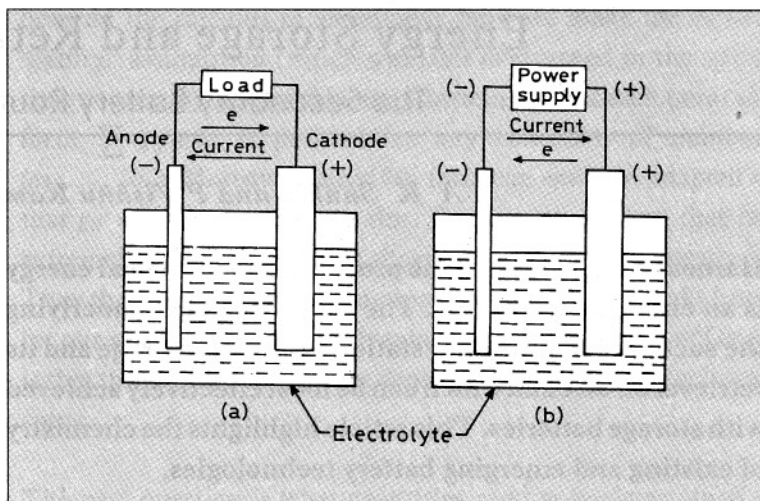
That is, they use chemical reactions to produce electricity. Such electrochemical devices are called *galvanic cells* in contrast to *electrolytic cells* which consume electrical energy to bring about a chemical reaction.

A battery consists of two electrodes, an anode and a cathode, and an electrolyte through which electrically charged particles can move (*Figure 1*). Two chemical reactions take place at the same time. The reaction taking place at the anode is an oxidation reaction of the type $R \rightarrow O + ne$, where R is the reduced species and O, the oxidised species. Such a reaction leads to an excess of electrons, ne, at the anode. It is also called the negative (–ve) electrode. The chemical reaction taking place at the cathode is a reduction reaction of the type $O' + ne \rightarrow R'$, which results in a depletion of electrons. Therefore the cathode is also called the positive (+ve) electrode. For example in a nickel-cadmium battery, Cd is oxidised to Cd^{2+} at the anode and Ni^{3+} is reduced to Ni^{2+} at the cathode and the reactions can be represented as

$$Cd \rightarrow Cd^{2+} + 2e \quad \text{at anode (–ve electrode),}$$
$$Ni^{3+} + e \rightarrow Ni^{2+} \quad \text{at cathode (+ve electrode).}$$
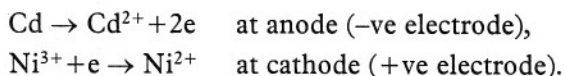
When the battery is connected to an external circuit (load), the excess electrons from the anode flow through the circuit and back

Table 1. Desirable features in a battery		
Battery performance parameter	**Definition**	**Desired target**
Energy density	Energy (stored) per kilogram of battery weight (Wh kg^{-1}) or per litre of battery volume (Wh l^{-1})	HIGH
Power density	Ratio of power available from a battery to its weight (W kg^{-1}) or volume (W l^{-1})	HIGH
Self discharge	Loss of charge due to parasitic reactions between periods of use	LOW
Internal resistance	Sum of electrical (ionic and electronic) resistances of the battery components	LOW
Cycle life	Number of charge-discharge cycles over which the energy density can be sustained under specific conditions (applicable to a secondary battery)	HIGH
Efficiency	Ratio of the charge output to the charge input during a charge-discharge cycle for a secondary battery	HIGH

to the cathode. As the electrons move through the circuit they lose energy. This energy may be used to create heat or light as in an electrical heater or light bulb, or to do work as in a motor. The flow of electrons results in a *current* and by convention the direction of flow of current is taken as opposite to the direction of flow of electrons. The energy released per unit charge while the current flows through the circuit is called *voltage*. The product of the current and the voltage is the *power* delivered to the circuit. When a battery delivers electric current to an external load, certain active materials in the battery are chemically converted into other materials at lower energy states and the battery is eventually fully discharged.

The battery most commonly known to us is the dry cell, which we use in our transistor sets or torches. These are purchased in their charged state and discharged through use and then discarded.

Table 2. Target characteristics for a high performance battery		
Performance parameter	Long life type	High energy density type
Weight energy density (Wh kg^{-1})	120	180
Wolume energy density (Wh l^{-1})	240	360
Cycle life	3500	500
Efficiency (%)	>90	>85

Others: Environmental stability, safety, easy maintenance, high range of operational temperature (–20 to 50^0 C), compactness, ruggedness and low cost.

Primary and Secondary Batteries

The battery most commonly known to us is the dry cell, which we use in our transistor sets or torches. These are purchased in their charged state and discharged through use and then discarded. Such cells are known as *primary cells*. They are of limited use as they deliver much less energy than what is required to construct them. Besides, the growing need for recycling resources requires that the discharged battery should be reusable a large number of times. In other words, we look for a *secondary* (rechargeable) or storage battery with a long *cycle life*. A secondary cell after discharge can be recharged by passing electric current through it in the reverse direction (*Figure 1*). During recharge it behaves like an electrolytic cell and converts electrical energy into chemical energy and the active electrode material is retrieved.

A high performance battery should have a maximum energy density at an optimum power density (rate of discharge), minimum internal resistance, maximum charge retention, mechanical strength and a long cycle life(see *Table 1*). The target values for all these parameters which would help define a high performance battery are given in *Table 2*.

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How Do We Construct a Battery?

A battery basically consists of two electrodes, at each of which a chemical reaction takes place. Every chemical reaction is associated with a certain free energy change, ΔG^0 (under standard conditions), which can be characterised by a potential E^0, such that $\Delta G^0 = -nFE^0$ (where n is the number of electrons involved in the reaction and F, the Faraday constant). This potential is called the single electrode potential. In a battery, the single electrode potentials of the two electrodes differ from one another so that electrons are released at the anode at a high energy. The electrons pass through a load and lose energy and are consumed at the cathode at a lower energy.

From the 100 odd elements known to us in the periodic table, nearly 5000 (i.e., $100\,´99/2$. The number is larger if variable oxidation states of some elements are taken into account.) pairwise combinations of single electrode reactions involving stable reactants and products can be theoretically envisaged. This leads to a similar number of different possible electrochemical energy storage systems. However in practice, more than a century of effort in the development of batteries has resulted in only a few systems of practical importance.
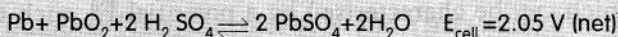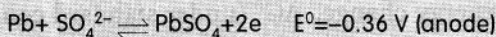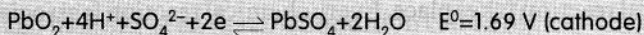
The small number of successful systems compared to the large number possible in theory suggests that a workable electrochemical energy storage system is critically dependent on several factors. Two obvious factors are cost and availability of required materials. In addition, a few factors related to the chemistry of the electrode materials play an important role.

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Chemistry of Reversible Electrodes

The electrode materials in a rechargeable or secondary battery must undergo a reversible chemical reaction. A typical electrode reaction can be schematically written as

$$M^{z+} \rightleftharpoons M^{(z+\Delta)+} + \Delta e \qquad (I)$$

Table 3. Electrode reactions in different batteries. E^0 values have been given where they are known. Arrows pointing to the right ($\rightarrow$) correspond to the discharge reactions and arrows pointing to the left ($\leftarrow$) correspond to the charging reactions. Advantages and disadvantages of the batteries are also given.
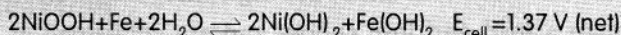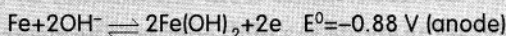
> **Table 3. Electrode reactions in different batteries.**
>
> - **Lead acid battery**
>
> $PbO_2+4H^++SO_4^{2-}+2e \rightleftharpoons PbSO_4+2H_2O$ $E^0=1.69$ V (cathode)
> $Pb+ SO_4^{2-} \rightleftharpoons PbSO_4+2e$ $E^0=-0.36$ V (anode)
> $Pb+ PbO_2+2 H_2SO_4 \rightleftharpoons 2 PbSO_4+2H_2O$ $E_{cell}=2.05$ V (net)
> *Low energy density, high Pb toxicity, corrosive but rugged*
>
> - **Nickel-iron battery**
>
> $2NiOOH+2H_2O+2e \rightleftharpoons 2Ni(OH)_2+2OH^-$ $E^0=0.49$ V (cathode)
> $Fe+2OH^- \rightleftharpoons 2Fe(OH)_2+2e$ $E^0=-0.88$ V (anode)
> $2NiOOH+Fe+2H_2O \rightleftharpoons 2Ni(OH)_2+Fe(OH)_2$ $E_{cell}=1.37$ V (net)
> *Poor performance of Fe electrode, not maintenance-free*
>
> - **Nickel-cadmium battery**
>
> $2NiOOH+2H_2O+2e \rightleftharpoons 2Ni(OH)_2+2OH^-$ $E^0=0.49$ V (cathode)
> $Cd+2OH^- \rightleftharpoons Cd(OH)_2+2e$ $E^0=-0.76$ V (anode)
> $2NiOOH+Cd+2H_2O \rightleftharpoons 2Ni(OH)_2+Cd(OH)_2$ $E_{cell}=1.25$ V (net)
> *High Cd toxicity but maintenance-free*
>
> - **Nickel-zinc battery**
>
> $2NiOOH+2H_2O+2e \rightleftharpoons 2Ni(OH)_2+2OH^-$ $E^0=0.49$ V (cathode)
> $Zn+2OH^- \rightleftharpoons ZnO+ H_2O+2e$ $E^0=-1.24$ V (anode)
> $2NiOOH+H_2O+Zn \rightleftharpoons 2Ni(OH)_2+ZnO$ $E_{cell}=1.73$ V (net)
> *Low cycle life but cost effective*
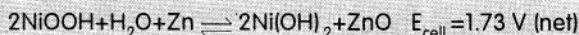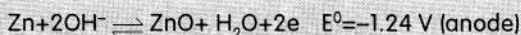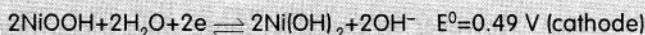
We must develop new batteries with enhanced performance characteristics for communication, space, automotive, and traction purposes.
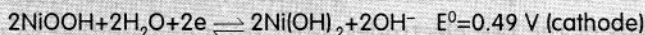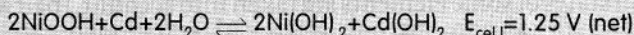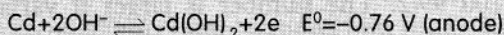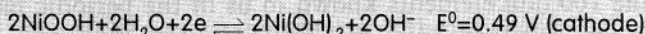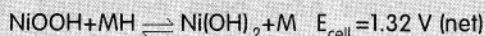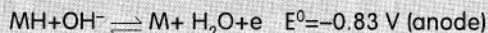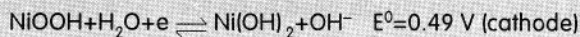
Here M is a metal ion and $z+$ and $(z+\Delta)+$ are its two oxidation states. For a material to qualify as a reversible electrode for secondary batteries it should satisfy the following conditions:

- As seen from reaction (I), the metal ion must be capable of adopting at least two oxidation states. This criterion is satisfied by many d-block elements.
- There should be a suitable chemical matrix that can host the metal ion in its multiple oxidation states. An oxide/hydroxide matrix is found to serve this purpose ideally although many sulphides are as good.
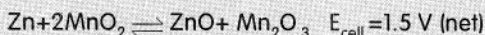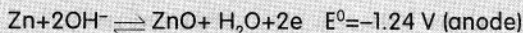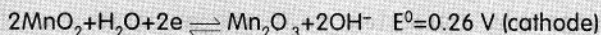- The reaction (I) must have a high degree of reversibility which

- Nickel-metal hydride battery

$NiOOH + H_2O + e \rightleftharpoons Ni(OH)_2 + OH^-$ $E^0 = 0.49$ V (cathode)

$MH + OH^- \rightleftharpoons M + H_2O + e$ $E^0 = -0.83$ V (anode)

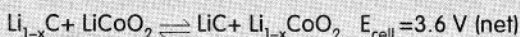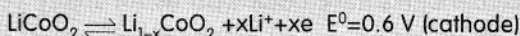$NiOOH + MH \rightleftharpoons Ni(OH)_2 + M$ $E_{cell} = 1.32$ V (net)

High cycle life, high energy density, non-toxic, maintenance free
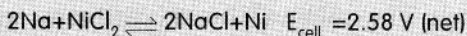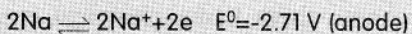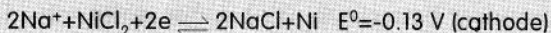
- Rechargeable alkaline manganese dioxide battery

$2MnO_2 + H_2O + 2e \rightleftharpoons Mn_2O_3 + 2OH^-$ $E^0 = 0.26$ V (cathode)

$Zn + 2OH^- \rightleftharpoons ZnO + H_2O + 2e$ $E^0 = -1.24$ V (anode)

$Zn + 2MnO_2 \rightleftharpoons ZnO + Mn_2O_3$ $E_{cell} = 1.5$ V (net)

Shallow discharge but cost effective

- Lithium ion rechargeable battery

$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe$ $E^0 = 0.6$ V (cathode)

$Li_{1-x}C + xLi^+ + xe \rightleftharpoons LiC$ $E^0 = -3.0$ V (anode)

$Li_{1-x}C + LiCoO_2 \rightleftharpoons LiC + Li_{1-x}CoO_2$ $E_{cell} = 3.6$ V (net)

High energy density, high cycle life, maintenance free but uneconomical

- Zebra battery

$2Na^+ + NiCl_2 + 2e \rightleftharpoons 2NaCl + Ni$ $E^0 = -0.13$ V (cathode)

$2Na \rightleftharpoons 2Na^+ + 2e$ $E^0 = -2.71$ V (anode)

$2Na + NiCl_2 \rightleftharpoons 2NaCl + Ni$ $E_{cell} = 2.58$ V (net)

High temperature operation, still in development stages

> The manner in which we are using secondary batteries today has not really solved the energy problem. The real breakthrough will come when advances in photovoltaics will enable us to recharge our secondary batteries by using solar energy.

is possible when neither the oxidised nor the reduced form is specially stable compared to the other. This is a difficult criterion to satisfy and only a few metals such as Pb, Mn, Ni and Co appear to pass this test.

- Both the reduced and oxidised forms of the material must have a fair degree of electrical conductivity or else the material will be rendered electrochemically inactive.

- Reaction (I) should have no competing reactions that produce electrochemically inactive side products which can reduce the activity of the electrode.

Several batteries have been in use commercially for a number of

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years. However, over the last two decades new applications and requirements have arisen which need to be met. As a result some old systems have declined in importance while others have expanded and new concepts have been developed. The commerically viable systems are: Lead-acid batteries, nickel-iron, nickel-cadmium, nickel-zinc, nickel-metal hydride, rechargeable alkaline manganese dioxide-zinc batteries, lithium ion rechargeable batteries and zebra batteries. The electrochemistry of these batteries is summarised in *Table 3.*

Future Prospects

Various battery technologies have been with us for many years. Technology dissemination and acceptance is no more a problem; in fact many new applications are crying out for the rapid development of new batteries with enhanced performance characteristics especially for communication, space, automotive, and traction purposes. Over the years many types of batteries have become commercially available. But the manner in which we are using secondary batteries today has not really solved the energy problem, as we recharge them using electrical energy obtained from fossil fuels. The real breakthrough will come when advances in photovoltaics will enable us to recharge our secondary batteries by using solar energy. By then battery technologists must be ready with high performance, cost effective, environment friendly and socially acceptable batteries.

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Suggested Reading

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