Abstract

A battery is a companion whose interests are world-wide and whose society has never-ending interests. Batteries have applications in cars to space and there is ever growing addiction to batteries. A battery consists of two electrodes, an anode and a cathode, and an electrolyte through which electrically charged particles but not electrons or reactants can move. Two chemical reactions take place at the same time. The reaction taking place at the anode is an oxidation reaction which results in generation of electrons while the chemical reaction taking place at the cathode is a reduction reaction which results in the depletion of electrons. Accordingly, the anode and cathode of the battery are also referred to as negative and positive plates. When the battery is connected to an external circuit, the excess electrons from the anode flow through the circuit and back 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 the current is opposite to the direction of flow of electrons. The energy which the electrons lose as they move through the circuit is called voltage. The product of the current and the voltage is power delivered to the circuit. When a battery delivers electric current to an external load, certain active materials in the battery are converted into other materials at lower energy states and the battery is eventually discharged. During recharge, a storage battery behaves like an electrolytic cell where the active electrode materials are retrieved.

It is desirable that the energy delivered by a battery during discharge should be as high as possible. The energy output of a battery is dependent on the amount of active material present in the battery. Since the weight and volume of the battery are at premium for most of the applications, it is the energy density which has to be maximized. Engineers refer to the quantity of electricity stored per kilogram of the battery as the energy density; the speed of delivery or rate of discharge is called power density. For many applications, such as traction and automotive, it is also necessary to have a high-power density. However, the energy density tends to decrease with an increase in power density because at high rates of discharge, a part of the energy is irreversibly lost as heat in the system. For an efficient delivery of charge from a battery, it is desirable that, the energy density be maximized at optimum required power.

Between periods of use, a loss in the available energy of the battery occurs partly due to a leakage of charge between the electrodes and partly due to consumption of charge at the electrodes by the parasitic reactions. This is commonly referred to as self-discharge. This results in a decrease in both the effectiveness of the battery as a source of energy and also its reliability for a given application during storage. Structural integrity of the battery is another important characteristic since this confers immunity from mechanical stresses such as vibrations and shocks to which batteries are often subjected in practice. In short, a maximum energy at optimum power density, minimum internal resistance, maximum charge retention, mechanical strength and long cycle-life are the desirable characteristics of a battery.

From the 100 odd elements in the periodic table, nearly 5000 pair-wise combinations of single electrode reactions involving stable reactants and products can be theoretically envisaged leading to a like number of electrochemical cells. In practice, however, more than a century of effort in the development of storage batteries has resulted in only a few systems of practical importance. The small number of successfu1 systems compared to large number possible in theory suggests that a workable battery is critically dependent on several factors. Two obvious factors, besides those related to chemistry of the electrode materials, are cost and availability of the materials. Starting from the lead-acid and Edison batteries, phenomenal advances have been made in storage battery technology. The most ubiquitous storage battery is the lead-acid battery which is one of the most successful electrochemical systems ever developed. Although it was first demonstrated by Planté as early as 1859 and many other storage batteries have been developed since, the lead-acid battery is still the most widely used storage battery. The key issues which prohibit lead-acid battery capture bigger markets are its short life and inadequate energy density in addition to safety, environmental impact and recyclability. It is these issues that have led to the emergence of nickel-cadmium batteries which exhibit compelling performance but suffer from the memory effect, a phenomenon that burdens the user with having to at least occasionally follow a time-consuming recharging regime in order to maintain their rated capacity. Besides, cadmium is an awful poison that can contaminate the environment. The unpopularity of cadmium has encouraged the development of the nickel-metal hydride (Ni-MH) batteries that are not only cadmium free but also can store more energy than comparably sized nickel-cadmium units. On the downside, they deliver less power, have a faster self- discharge rate and less tolerant to overcharge like the nickel-cadmium cell. The solution to the aforesaid problems lies in replacing cadmium with iron as in a Ni-Fe battery that has advantages in cost, calendar life, environmental safety, and robustness.

In hibernation for decades, the nickel-iron system has begun to catch the attention of policy makers in recent years. The resurrection of the system rests heavily on its techno-economic feasibility for a number of applications arising out of recent technological developments. Two problem areas that are being addressed are: (i) catalytic recombination of hydrogen and oxygen gases that are evolved in the battery, with possibilities of a sealed battery, and (ii) electrode/electrolyte additives that can shift the overvoltage for the hydrogen evolution reaction (HER). Latching on to the new developments should propel nickel-iron battery for applications wherefrom nickel-cadmium batteries have been withdrawn. Its cost competitiveness is obvious considering its longevity, typically 3,000 cycles, corresponding to a calendar life of about 20 years. Particular areas of application should include stationary ones as in photovoltaic installations, where its mechanical robustness and long life, even under adverse operational conditions such as over-charge, over-discharge, charge-stand, discharge-stand and inadequate maintenance would be very attractive.

The discharge reactions of the iron electrode proceed in two steps, yielding $Fe(OH)_2$ in the first discharge step and Fe_3O_4 in the second. The open-circuit potential of the charged alkaline iron electrode is always cathodic to the potential for HER in the same solution, which renders the metal thermodynamically unstable. But the extraordinary robustness and service life are compelling for civilian applications. The nickel cathode is a well-established system. Under

shallow discharge regimes, the nickel electrode is known to sustain more than 20,000 cycles as in Super Ni-Cd batteries for space applications. The degree of utilization of the nickel electrode varies from about 60% for pocket plate or pressed plate electrodes to more than 90% for sintered plate electrodes. Freshly charged nickel electrodes lose 0.1–0.2% capacity a day by self-discharge at 25°C, which may be reduced with additives such as CdO; cycling the iron electrode is fraught with problems of poor charging efficiency (50–70%) and low electrode utilization. Accordingly, to offset the loss and to achieve satisfactory performance, iron electrodes are typically overcharged by 60–100%.

Recently, the beneficial effect of sulfide additives on the cyclability of the iron electrodes has been demonstrated, with a utilization efficiency of 68% of the rated capacity at 1C rate. However, full exploitation of the system rests on control of the wasteful evolution of hydrogen during charging. It was also shown that *in situ* electro-deposited bismuth led to substantial inhibition of the kinetics of HER. The hydrogen evolution that occurs during charging lowers the round-trip energy efficiency and necessitates constant maintenance to replenish lost water. The gas evolution would mean that the battery cannot be sealed. Carbonation of the electrolyte is thus a serious concern. It is clear, therefore, that suppression of the evolution of hydrogen and sealability of the nickel-iron system have far-reaching ramifications not only in raising the overall energy efficiency and lowering the cost, but also in facilitating its penetration in various spheres of application. Recently, a nickel-iron cell with a recombination catalyst was reported that paves the way for the development of a sealed version of the battery.

Another concern with these batteries is their poor high-rate discharge performance. Several applications such as electric vehicles and grid-scale energy storage demand battery discharge at C or C/2 rates. It is found that a combination of high-purity α-iron incorporated with bismuth by electro-reduction of bismuth sulphide exhibits a ten-fold decrease in hydrogen evolution rate without interfering with the kinetics of the iron electrode reactions. It is reported that an unprecedented 96% charging efficiency at a specific capacity of 300 mAh g^{-1} for the iron electrode and a twenty-fold increase in capacity at C/2 rate is now achievable. These breakthroughs in the technology of the alkaline iron electrode should augur well for large-scale exploitation.

Recently, a nickel-iron battery with iron oxide grown on graphene as the anode and nickel hydroxide deposited on multi-walled carbon nanotubes as the cathode is constructed. The nano-configuration displayed a dramatic improvement in performance: it could be fully charged in about two minutes and discharged in less than 30 seconds. This is a jump of more than 1,000 times over the conventional rates of charging and discharging. The new nano-material-based technology opens up opportunities especially in electric traction. Because the battery allows fast charging and discharging, one would be tempted to put it to more frequent use, like a supercapacitor.

In recent years, interest in nickel-iron batteries is being revived since these batteries are reliable and inexpensive, can be subjected to high discharge rates, exhibit good low- and high-temperature behavior with long cycle life, can undergo two-step charge-discharge, can provide reserve charge during the second step of discharge, are electrically and mechanically rugged, and, above all, are environment-friendly. Today, it looks even feasible to assemble nickel-iron batteries in sealed form by incorporating a gas-recombination catalyst. In brief, the development of a commercially viable nickel-iron battery looks compelling provided the underlying problems are sorted out.

In the light of the foregoing, a novel rechargeable iron electrode for nickel-iron batteries is developed and studied in this thesis. The thesis comprises five chapters. After a brief introduction to rechargeable iron electrodes for nickel-iron batteries, the second chapter of the thesis describes studies on iron electrodes prepared from carbonyl iron powder. In this study, we have demonstrated iron electrodes prepared from carbonyl iron powder (CIP) that are capable of delivering a specific discharge capacity of about 400 mAh g^{-1} at a current density of 100 mA g^{-1} with a faradaic efficiency of about 80%. The specific capacity of the electrodes increases gradually during formation cycles and reaches a maximum in the 180th cycle. The slow increase in the specific capacity is attributed to the low surface-area and limited porosity of the pristine CIP. Evolution of charge potential profiles is investigated to understand the extent of charge acceptance during formation cycles. *In situ* X-ray diffraction (XRD) pattern for the electrodes subsequent to 300 charge/discharge cycles confirms the presence of Fe with Fe(OH)2 as dominant phase. In the third chapter of the thesis, studies on an *in-situ* carbon-grafted alkaline iron electrode prepared from the active material obtained by decomposing α-FeC2O4·2H2O– polyvinyl alcohol (PVA) composite at 600°C in vacuum is reported. The active material comprises a mixture of α-Fe and Fe3O4 with the former as the prominent component. A specific discharge capacity in excess of 400 mAh g^{-1} at a current density of 100 mA g^{-1} is obtained with a faradaic efficiency of 80% for the iron electrode made from carbon-grafted active material·10 (CGAM·10). The enhanced performance of the alkaline iron electrode is attributed to the increased amount of metallic iron in the active material and its concomitant *in situ* carbon grafting. In chapter 4 of the thesis, the beneficial effects of carbon grafting into the iron active material for rechargeable alkaline-iron-electrodes with and without Bi2S3 additive is probed by *in situ* X-ray diffraction in conjunction with Extended X-ray Absorption Fine Structure (EXAFS) and electrochemistry. EXAFS data unravel that the composition of pristine active material (PAM) for iron electrodes comprises 87% of magnetite and 13% of α-iron while CGAM·10 comprises 60% of magnetite and 40% of α-iron. *In situ* XRD patterns are recorded using a specially designed electrochemical cell. XRD data reflect that magnetite present in PAM iron electrode, without bismuth sulfide additive, is not reduced during charging while PAM iron electrode with bismuth sulfide additive is partially reduced to α-Fe/Fe(OH)2. Interestingly, carbon-grafted-iron electrode with bismuth sulfide exhibit complete conversion of Fe3O4 present in the active material to α-Fe/Fe(OH)2. The ameliorating effect of carbon grafting is substantiated by kinetic parameters obtained from steady state potentiostatic polarization and Tafel plots. The mechanism for iron-electrode charge – discharge reactions are discussed in the light of the potential – pH diagrams for Fe – H2O, S – H2O and FeSads – H2O systems and it is surmised that carbon grafting into iron active material promotes its electrochemical utilization. Final chapter (Chapter 5) of the thesis

describes a study on a 12 Ah positive–limited nickel-iron cell with sintered-nickel electrodes and roll-compacted carbon-grafted iron electrodes. The cell is performance tested by subjecting it to galvanostatic charge/discharge cycles. It is found that the cell retains about 93% of its initial capacity after 100 cycles. It is surmised that shedding of the negative plate is primarily responsible for the observed capacity decay in the cell.

Batteries are energy devices, and as energy and power play against each other, increasing one will lead to a loss in the other. This means that if we require high power from a battery, we will extract less total energy than when we require low power. Capacitors complement battery power by allowing very rapid charge and discharge. Accordingly, capacitors will gel well with batteries into the emerging energy-storage landscape. Since the capacitance mode allows storage of electricity directly as electrical charges, electrical-double-layer capacitors can have efficiencies close to 100%. Keeping this in mind, a proof-of-concept study on iron-carbon hybrid capacitor has been conducted and is described in appendix of the thesis.

It is hoped that the studies reported in the thesis would constitute a worthwhile contribution to science and technology of nickel-iron accumulators. It would not be an exaggeration to add that, considering the need, availability, cost and safety, nickel-iron accumulators are set to play a central role in future energy storage and management.