

ABSTRACT

The commercialization of Li-ion battery (LIB) in 1990s by Sony Corporation has led to its applications in portable electronic devices such as mobile phones, cameras, laptop computers, etc. Initially, the energy density of commercial LIB was only about 120 Wh Kg⁻¹. However, with sustained improvements in properties of various cell components, the present-day LIB provides energy density of about 250 Wh Kg⁻¹. With future use envisaged for mobility applications such as electric vehicles, research activities have gained momentum for development of high energy density Li-S and Li-O₂ batteries. However, due to limited sources of lithium (0.007 % in earth's crust and 0.2 ppm in sea water) and uneven distribution, concerns arise about its cost and availability which would inhibit bulk production and utilization of lithium-based batteries. Hence, there is an urgent need to switch over to battery systems employing earth abundant and environmentally benign materials.

Sodium and potassium-based batteries have received attention in research laboratories as alternatives to lithium-based batteries due to their natural abundance and low cost. Na and K are the metals below Li in the periodic table and their physical and chemical properties are similar to those of Li. Na and K are the sixth and seventh most abundant elements, constituting 2.6 % and 2.4 %, respectively of the earth's crust. Sea water contains about 10800 ppm Na and 400 ppm K. Although, the standard potentials of Na/Na⁺ (-2.71 V vs. standard hydrogen electrode (SHE)) and K/K⁺ (-2.93 V vs. SHE) are less than Li/Li⁺ (-3.04 V vs. SHE) by about 300 and 100 mV, respectively, the cost and availability factors outweigh the marginal reduction in energy density. The quest for new electrode materials for Na- and K-based batteries, their physicochemical characterizations and electrochemical investigations are described in the thesis.

It consists of a comprehensive review of the literature on the evolution of battery systems with a focus on the next generation Na- and K-based batteries. The cathode and anode materials for Na- and K-ion batteries are reviewed along with the current research activities in Na- and K-sulphur, and Na- and K-O₂ batteries.

It furnishes a brief description of various experimental techniques and procedures adopted at different stages of the present thesis.

The amorphous MnO₂ has been prepared by two different methods: (i) reduction of KMnO₄ using ethylene glycol (EG) and (ii) the redox reaction between KMnO₄ and MnSO₄.H₂O at ambient conditions. The as prepared MnO₂ samples in both cases are amorphous in nature and on heating in the temperature range of 300 – 800 °C, they convert to α-MnO₂. The MnO₂ prepared by reduction by EG has been studied for Na/MnO₂ and Li/MnO₂ laboratory scale primary cells in non-aqueous electrolytes. The specific capacity of amorphous MnO₂ is 300 mAh g⁻¹ in both Na/MnO₂ and Li/MnO₂ cells. Na/MnO₂ cell shows a nominal voltage less than Li/MnO₂ cell by 0.35 V, as expected. MnO₂ prepared by the redox reaction between KMnO₄ and MnSO₄.H₂O has a specific surface area of 184 m² g⁻¹ with narrowly distributed mesopores of 3.5 nm pore diameter. The crystallinity increases and specific surface area decreases upon heating. The as prepared sample provides the first discharge capacity of about 300, 200 and 80 mAh g⁻¹ for Li-, Na- and K-MnO₂ cells, respectively, at a specific current of 50 mA g⁻¹. The attractively high discharge capacity of the as prepared amorphous MnO₂ is

attributed to the large specific surface area and mesoporosity. However, the crystalline samples exhibit low specific discharge capacity in comparison with amorphous samples.

It deals with electrochemical impedance spectroscopy (EIS) study of Na/MnO₂ primary cell fabricated in a non-aqueous electrolyte of Na salt. The EIS data provides a high resistance of Na metal due to the surface passive film. On subjecting the cell for discharge, the surface film causes a delay response of the cell voltage and the closed-circuit voltage reaches the normal discharge level following dielectric break-down of the film. The EIS data measured at different stages of cell discharge are subjected to non-linear least squares fitting with the aid of an appropriate equivalent circuit. The impedance parameters are examined to throw light on state-of-charge of Na/MnO₂ primary cells. The study has been further extended to analyze the delay-time behaviour of the non-aqueous Na/MnO₂ cells and quantifying the film resistance and break-down field for the film formed on the Na surface.

P2-type Na_{0.67}Mn_{0.65}Fe_{0.20}Ni_{0.15}O₂ is studied as a cathode material for Na-ion battery and presented. It is synthesized in microspherical and disc-like morphologies using two different synthetic procedures. Microspheres of FeCO₃ are first prepared and used as a template to synthesize Mn_{0.65}Fe_{0.20}Ni_{0.15}CO₃, followed by its thermal decomposition to the corresponding oxide and finally, thermal fusion of the oxide with Na₂CO₃ to produce P2-type Na_{0.67}Mn_{0.65}Fe_{0.20}Ni_{0.15}O₂. However, disc-like Na_{0.67}Mn_{0.65}Fe_{0.20}Ni_{0.15}O₂ is synthesized by sintering the product obtained using a low temperature solution combustion method using aqueous solution of stoichiometric quantities of corresponding metal nitrates and sucrose as the fuel at 800 °C. Cyclic voltammograms in both the samples are characterized by well-defined two pairs of current peaks corresponding to the oxidation and reduction processes in two different stages. The sodiated microspherical oxide provides an initial discharge capacity of about 216 mAh g⁻¹ at C/15 rate cycling with an excellent cycling stability (Fig. 3a). The rate capability is also high, and the discharge capacity is about 100 mAh g⁻¹ at 2C rate. The high discharge capacity and high rate capability are attributed to porous microspherical morphology. When the cells with disc-like morphology cathode sample are cycled at a current density of 35 mA g⁻¹, a specific discharge capacity of 178 mAh g⁻¹ is obtained with close to 100 % coulombic efficiency. Capacity retention of more than 70 % is observed after 50 charge-discharge cycles

Potassium tetratitanate (K₂Ti₄O₉) is synthesized by solid-state method using K₂CO₃ and TiO₂ and studied as an anode material for potassium ion batteries (KIB) for the first time. A discharge capacity of 97 mAh g⁻¹ has been obtained at a current density of 30 mA g⁻¹ (0.2 C rate) and 80 mAh g⁻¹ at 100 mA g⁻¹ (0.8 C rate), initially (Fig. 4a). The proposed mechanism of charging involves reduction of two Ti ions from 4+ oxidation state to 3+ oxidation state, which facilitates insertion of two K⁺ ions per formula unit in the zig-zag layer of TiO₆ octahedra separated with K⁺ ions with interlayer spacing of 0.85 nm. For KIB cathode, K_{0.27}Mn_{0.65}Fe_{0.35-x}Ni_xO₂ (0.00 ≤ x ≤ 0.35) is synthesized in microspherical morphology. The potassiated mixed metal oxide formed in microspherical morphology is in pure crystalline phase. The oxide with the composition x = 0.35 i.e., K_{0.27}Mn_{0.65}Ni_{0.35}O₂ provides the highest first specific discharge capacity of 97 mAh g⁻¹ at C/10 rate (Fig. 4b). A good cycling stability is observed.

It deals with carbonization of milk-free coconut kernel pulp carried out at low temperatures. The carbon samples are activated using KOH and electrical doublelayer capacitor (EDLC)

properties are studied (Fig. 5a). Among the several samples prepared, activated carbon prepared at 600 °C has a large specific surface area (1200 m² g⁻¹). Cyclic voltammetry and galvanostatic charge-discharge studies suggest that activated carbons derived from coconut kernel pulp are appropriate materials for EDLC studies in acidic, alkaline and non-aqueous electrolytes. Specific capacitance (SC) of 173 F g⁻¹ is obtained in 1 M H₂SO₄ electrolyte for the activated carbon prepared at 600 °C.

The supercapacitor properties of activated carbon sample prepared at 600 °C are superior to the samples prepared at higher temperatures. Electrochemical studies are also undertaken for the prepared and activated samples for sodium ion intercalation/deintercalation. It is found that various factors such as surface area, mesoporosity, inter-layer spacing, electrolyte diffusion, solid electrolyte interface formation for high surface area carbon, etc. contribute to the capacity and cycle life of the material. Carbon sample synthesized at 600 °C and having a specific surface area of about 280 m² g⁻¹ provides the highest discharge capacity of about 200 mAh g⁻¹ with good cycling stability. The thesis ends with a short summary and prospects of the investigations described here in. The work presented in it is carried out by the candidate as a part of Int. Ph.D. program. Some of the results are published in the literature and some more manuscripts are in preparation. A list of publications is enclosed. It is hoped that the studies reported in the thesis are worthy contributions.