Synopsis

Synopsis of the thesis entitled “Electrochemical supercapacitor investigations of MnO₂ and Mn(OH)₂” by Prasant Kumar Nayak (S. R. No: 4-04-06-1-04553-0) under the supervision of Prof. N. Munichandraiah, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-12, India, for the Ph.D., degree of the Institute under the Faculty of Science.

Electrical double-layer formed at the electrode/electrolyte interface in combination with electron-transfer reaction can lead to many important applications of electrochemistry, including energy storage devices, namely, batteries, fuel cells and electrochemical supercapacitors. Electrochemical supercapacitors are characterized by their higher power density as compared to batteries and higher energy density than the conventional electrostatic and electrolytic capacitors. Thus, supercapacitors are useful as auxiliary energy storage devices along with primary sources such as batteries or fuel cells for the purpose of power enhancement in short pulse applications. These are expected to be useful in hybrid devices together with batteries or fuel cells, in electric vehicle propulsion systems.

Among the various materials studied for electrochemical supercapacitors, carbonaceous materials, transition metal oxides and conducting polymers are important. Carbon in various forms is used as a double-layer capacitor material, which stores charge by electrostatic charge separation at the electrode/electrolyte interface. The specific capacitance (SC) of high surface area activated carbon is about 100 F g⁻¹ in aqueous electrolytes.

Transition metal oxides have attracted considerable attention as electrode materials for supercapacitors because of the following merits: variable oxidation state, good chemical and electrochemical stability, ease of preparation and convenience in handling. Hydrated RuO₂ prepared by sol-gel process exhibited a SC as high as 720 F g⁻¹. However, high cost, low porosity and toxic nature of RuO₂ limit its commercialization in supercapacitors. On the other hand, MnO₂ is an attractive electrode material as it is electrochemically active, cheap, environmentally benign, and its resources are abundant in nature. In an early report on the capacitance properties of MnO₂ by Lee and Goodenough [J. Solid State Chem. 144 (1999) 220], amorphous hydrous MnO₂ synthesized by co-precipitation method exhibited a SC of 203 F g⁻¹ in 2 M KCl
electrolyte. According to the charge-storage mechanism of MnO₂ involving MnO₂ + M⁺ + e⁻ ↔ (MnOO)M⁺ (where M⁺ = Li⁺, Na⁺, K⁺ etc.), a SC of 1110 F g⁻¹ is expected over a potential window of 1.0 V. However, SC values in the range of 100-200 F g⁻¹ are reported in the literature. The low values of SC are because of the charge-storage is confined to surface region of MnO₂ particles or films. It is desirable to enhance the SC of MnO₂ to a value close to the theoretical value. In view of this, attempts are made to enhance the SC of MnO₂ by adopting different synthetic procedures such as electrochemical method for depositing MnO₂ and also nanostructured mesoporous MnO₂ by polyol route, hydrothermal route and sonochemical method in the present studies. As the charge-storage mechanism of MnO₂ involves the surface insertion/deinsertion of cations from the electrolyte during discharge/charge processes, respectively, the capacitance properties of MnO₂ are studied in various aqueous electrolytes containing monovalent (Na⁺), bivalent (Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺) and trivalent (La³⁺) cations. The mass variation occurring at the electrode during the charge/discharge of MnO₂ is examined by electrochemical quartz crystal microbalance (EQCM) study. In addition to this, the kinetics of electrodeposition and capacitance properties of Mn(OH)₂ are studied by employing EQCM. Also, properties of asymmetric capacitors assembled with Mn(OH)₂ as the positive electrode and carbon as the negative electrode are studied and compared with symmetric Mn(OH)₂ capacitors. Furthermore, attempts are made to increase the potential window of Co(OH)₂ in alkaline and neutral electrolytes. The contents of the thesis by Chapter-wise are given below.

Chapter 1 introduces the importance of electrochemistry in energy storage and conversion, basics of electrochemical power sources, importance of some electroactive materials in electrochemical energy storage, different synthetic procedures for MnO₂ and its application in electrochemical supercapacitors. Transition metal oxides are widely studied because of their variable oxidation states, high electrochemical activity, abundance in nature and environmental compatibility. Various reports appeared in the form of open publications on supercapacitor studies of transition metal oxides such as RuO₂, MnO₂, Fe₃O₄, Co(OH)₂, Ni(OH)₂, NiO, etc., are briefly reviewed. The chapter ends with statements on objectives of the studies carried out and reported in the thesis.

Chapter 2 provides experimental procedures and methodologies used for the studies reported in the thesis. Different experimental routes adopted for synthesis of MnO₂, Mn(OH)₂
and Co(OH)$_2$ used for the studies are described. Also included are brief descriptions of various physicochemical and electrochemical techniques employed for the investigations.

In Chapter 3, MnO$_2$ samples synthesized by various routes such as electrochemical method, polyol route, hydrothermal route and sonochemical method are studied. MnO$_2$ and Mn(OH)$_2$ are simultaneously electrodeposited on the anode and the cathode, respectively, in a galvanostatic electrolysis cell consisting of aqueous Mn(NO$_3$)$_2$ electrolyte. MnO$_2$/SS and Mn(OH)$_2$/SS electrodes are used as the negative and the positive electrodes, respectively, in an asymmetric Mn(OH)$_2$/MnO$_2$ supercapacitor. MnO$_2$ samples are prepared at room temperature and in hydrothermal method at a temperature of 140 °C by reduction of KMnO$_4$ with poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG) or P123 as a reductant. Also, MnO$_2$ is prepared from KMnO$_4$ by hydrothermal method without using any reducing agent. This procedure requires a temperature of 180 °C and 24 h duration. MnO$_2$ is also synthesized with an ultrasonic aided procedure. The electrochemical capacitance properties of MnO$_2$ samples synthesized by various routes are investigated. A maximum SC of 264 F g$^{-1}$ is obtained at a current density of 0.5 mA cm$^{-2}$ (1.0 A g$^{-1}$) for MnO$_2$ prepared by sonochemical method.

The capacitance properties of MnO$_2$ are generally studied in neutral aqueous Na$_2$SO$_4$ electrolytes. In Chapter 4, electrolytes of NaNO$_3$, Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Sr(NO$_3$)$_2$, Ba(NO$_3$)$_2$ and also La(NO$_3$)$_3$ are studied and the results are compared with Na$_2$SO$_4$ electrolyte. Among the alkaline earth salt solutions, higher SC values are obtained in Mg(NO$_3$)$_2$ and Ca(NO$_3$)$_2$ electrolytes than in the rest of the electrolytes. Furthermore, MnO$_2$ exhibits capacitance behaviour in La(NO$_3$)$_3$ solution with enhanced SC in comparison with NaNO$_3$ and Mg(NO$_3$)$_2$ solutions. The SC increases with an increase in charge on the cation (Na$^+$, Mg$^{2+}$ and La$^{3+}$). The values of SC measured in Na$^+$, Mg$^{2+}$ and La$^{3+}$ electrolytes are 190, 220 and 257 F g$^{-1}$, respectively at a c.d. of 0.5 mA cm$^{-2}$ (1.0 A g$^{-1}$). Rate capabilities are also found to be different in different electrolytes. Specific energy and specific power are calculated and presented as Ragone plots. The presence of divalent and trivalent cations inserted onto MnO$_2$ is identified by X-ray photoelectron spectroscopy. EQCM is employed to monitor the increased mass variations that accompany reversible adsorption/desorption of Na$^+$, Mg$^{2+}$ and La$^{3+}$ ions onto MnO$_2$.

In Chapter 5, EQCM has been used to study the kinetics of electrochemical precipitation of Mn(OH)$_2$ on Au-crystal and its capacitance properties. From the EQCM data, it is inferred that
NO$_3^-$ ions get adsorbed on Au-crystal, and then undergo reduction resulting an increase in pH near the electrode surface. Precipitation of Mn$^{2+}$ occurs as Mn(OH)$_2$, resulting an increase in mass of the Au-crystal. On charging, Mn(OH)$_2$ undergoes oxidation to MnO$_2$, which exhibits electrochemical supercapacitor behaviour on subjecting to cycling in aqueous Na$_2$SO$_4$ electrolyte. EQCM data indicates the mass variations corresponding to surface insertion/extraction of Na$^+$ ions during discharge/charge cycling of Mn(OH)$_2$ in aqueous Na$_2$SO$_4$ electrolyte.

In Chapter 6, Mn(OH)$_2$ synthesized by precipitation of MnSO$_4$ with NH$_4$OH solution is studied for capacitance properties. A SC of 141 F g$^{-1}$ is obtained for the Mn(OH)$_2$ at a c.d. of 0.66 A g$^{-1}$ in 1.0 M Na$_2$SO$_4$ electrolyte in the potential range of 0-1.0 V vs. standard calomel electrode (SCE). Also, carbon electrode made from high surface area carbon exhibits a SC of 158 F g$^{-1}$ at a c.d. of 0.81 A g$^{-1}$ in the potential range of 0 to -1.0 V vs. SCE. Asymmetric capacitors are assembled by combining Mn(OH)$_2$ as the positive and carbon as the negative electrodes. The asymmetric capacitor has a SC of 39 F g$^{-1}$ at a c.d. of 0.42 A g$^{-1}$ in the operating voltage of 1.8 V. However, a symmetric capacitor consisting of two Mn(OH)$_2$ electrodes provides a SC of 11 F g$^{-1}$ only at a c.d. of 0.24 A g$^{-1}$ in an operating voltage of 1.2 V.

In Chapter 7, MnO$_2$ synthesized by reduction of KMnO$_4$ using ethylene glycol is used for fabrication of large area electrodes. Stainless steel (SS) mesh of 3 cm x 3 cm with geometrical area of 18 cm$^2$ is used as current collector. Three symmetrical electrochemical supercapacitors (capacitance of about 100 F per each at a current of 0.2 A) are assembled, each with 11 electrodes positioned in parallel. Six alternate electrodes are stacked as the negative terminal and the other five as the positive terminal. The electrochemical properties of MnO$_2$ supercapacitors are studied by galvanostatic charge-discharge cycling and ac impedance in 1.0 M Na$_2$SO$_4$ electrolyte. Also, the capacitors are combined in parallel as well as in series and the capacitance is evaluated. The practical application of the electrochemical supercapacitors is shown by demonstrating the running of a toy fan connected to the charged capacitor as well as the glowing of LED cell connected to charged supercapacitors connected in series. A parallel combination of batteries and capacitors is also demonstrated.

Capacitor studies of Co(OH)$_2$ over a limited potential window in alkaline electrolytes are reported in the literature. A high potential window of a capacitor material is desirable for using in a device. In Chapter 8, experiments are conducted to understand the reason for a low potential...
window for Co(OH)$_2$ as a capacitor material and also to increase its potential window. Experiments are conducted in aqueous NaOH and Na$_2$SO$_4$ electrolytes of various concentrations using electrochemically precipitated Co(OH)$_2$ on stainless steel current collectors in an aqueous Co(NO$_3$)$_2$ electrolyte. Based on the potential window, specific capacitance and specific energy, it is found that 0.05 M NaOH electrolyte is more appropriate for capacitor properties of Co(OH)$_2$ than the rest of the electrolytes studied. Using a Co(OH)$_2$ electrode with a specific mass of 1.0 mg cm$^{-2}$ in 0.05 M NaOH, a SC of about 380 F g$^{-1}$ is obtained with a potential window of 0.85 V at a charge-discharge c.d. of 10 A g$^{-1}$ (10 mA cm$^{-2}$).

The work presented in this thesis is carried out by the candidate as a part of Ph. D. training program and most of the results have been published in the literature. A list of publications of the candidate is enclosed below. It is hoped that the studies reported here will constitute a worthwhile contribution.

**List of publications:**