Abstract

Supercapacitors are a class of energy storage devices which rely on surface reactions in an electrochemical environment to store charges. These surface reactions involve forming a double layer of immovable electrostatic charges that is separated from the electrode by a few Å. Else it can also involve redox reactions at the electrode surface which is usually initiated by ions from the electrolyte. Supercapacitors takes small amount of time for their charging and discharging process, demonstrates high cyclic lifetime and has a high rate capacity. Supercapacitors can achieve a high power density which is ideally suited for applications where short burst of power is required. High electrode surface area can boost the capacitance, while use of neutral aqueous based, organic based and ionic liquid based electrolytes have shown to enhance the voltage capability of the supercapacitor which can drive up its energy density.

Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) are constituent reaction of electrochemical splitting of water (H_2O) molecule in the presence of a catalyst. These reactions form part of a promising water based energy cycle which can happen in an acidic or an alkaline environment. The role of electrocatalyst is vital in determining the potential and kinetics of these reactions. Electrocatalysts having metal ions high redox activity, high surface area and suitable binding energies of reaction intermediaries, and low toxicity are highly sought after for these aforementioned reactions.

Magnesium based metal oxides having one or more redox ions, with vacant/partially filled d-orbitals are suited for electrochemical applications. They present a viable choice for both supercapacitor as well electrocatalyst role and have been reported in scientific literature in such roles.

The present investigation is focused on synthesis of $MgAO_2$ (where A = Ni, Co) and $MgFe_2O_4$ electrode by different techniques. These electrode samples are suitable characterized to determine their material properties such as phase, microstructure, vibrational modes, electronic states and chemical bonds present in them. Thereafter these electrode materials are subjected to a series of electrochemical tests to assess their voltage window, charge storage process, the specific capacitance, the relaxation time, the energy density, the capacitance retention (for 1000 cycles), the HER and OER onset voltage, overpotential, fitted Tafel slopes, ECSA and catalytic stability. These tests help us to assess the performance of the electrode materials towards supercapacitor electrode using neutral aqueous electrolyte systems and alkaline electrocatalyst role.

Firstly, $MgNiO_2$ electrode is prepared by sol-gel method and named as MNO-3. The sample had spherical particle with 40-50 nm diameter. Supercapacitor performance of MNO-3 electrode in Li-ion based (1 M Li_2SO_4) electrolyte revealed a specific capacitance of 30 F/g (put through 0.5 A/g current density), energy density of 20 Wh/kg and 88.12% capacitance retention (exposed to 1.5 A/g current density). In Na-ion based (0.5 M Na_2SO_4) electrolyte, MNO-3 electrode demonstrated a specific capacitance of 34 F/g (put through 0.5 A/g current density), energy density of 23 Wh/kg and capacitance retention of 87.38% (exposed to 2 A/g current density). Using Mg-ion (1 M $Mg(ClO_4)_2$) electrolyte, MNO-3 electrode displayed a specific capacitance of 26 F/g (put through 0.5 A/g current density), energy density of almost 17 Wh/kg and 87.43% capacitance retention (exposed to 2 A/g current density).

Next, $MgNiO_2$ sample was prepared by molten-salt method. The sample was named MNO-1 and it was found to be composed of octahedron shaped particles with a 550 nm diameter on average. In Na-ion electrolyte (0.5 M Na_2SO_4), the sample exhibited a specific capacitance of 76 F/g (put through current density of 0.75 A/g), capacitance retention of 88.3% (exposed to 1.5 A/g current density) and energy density of almost 51 Wh/kg. MNO-1 sample using alkaline (1 M KOH) electrolyte demonsrated -0.636 V (vs. R.H.E) HER onset voltage, 636 mV overpotential, and 222.05 mV/dec Tafel slope. It also exhibited 56.75 cm^2 ECSA and a very steady current response for 5 h duration with a minor reduction of 6 mV overpotential.

Then $MgCoO_2$ sample was prepared via sol-gel method and called MCO-3. The sample had particles with an irregular cuboidal shape whose diameter is 260 nm on average. MCO-3 sample displayed a specific capacitance of 56 F/g (put through 0.5 A/g applied current density), energy density of 38 Wh/kg, 92.53% capacitance retention (exposed to 5 A/g applied current density) using Li-ion electrolyte (1 M Li_2SO_4). In Na-ion electrolyte (1 M $NaClO_4$), the sample displayed a specific capacitance of 47 F/g (under 0.5 A/g applied current density), energy density of almost 31 Wh/kg, capacitance retention of 91.41% (under 3.5 A/g current density). For HER application in KOH electrolyte, MCO-3 realized a HER onset at -0.4 V (vs. R.H.E) and achieved an overpotential of 400 mV, in addition to a fitted Tafel slope of 174 mV/dec. The sample further showed an ECSA of 46 cm^2 and a high degree of stability in current response for 5 h cycling with a minor drop in overpotential by 20 mV.

Lastly $MgFe_2O_4$ sample was fabricated using sol-gel method. The sample was named MFO-1 and it constituted of spherical nanoparticles with almost 47 nm diameter on average. MFO-1 sample achieved a specific capacitance of 61 F/g (exposed to 0.5 A/g applied current density), capacitance retention of 82.91% (put through 2.25 A/g current density) and energy density of 41 Wh/kg in conjunction with Na-ion electrolyte (1 M $NaClO_4$). In Mg-ion electrolyte (1 M $Mg(ClO_4)_2$), the sample achieved a specific capacitance of 43 F/g (put through a current density of 0.75 A/g), 82.15% capacitance retention (exposed to 1.5 A/g applied current density) and 29 Wh/kg energy density. In KOH electrolyte, the sample showed an OER onset at 2.32 V (vs. R.H.E), 1.09 V overpotential, and 317 mV/dec calculated Tafel slope. The sample obtained 10.225 cm^2 ECSA and a steady OER response for 5 h duration with a minor reduction of overpotential by 22 mV. HER experiments on MFO-1 revealed HER onset at -0.402 V (vs. R.H.E), a calculated overpotential of 402 mV, fitted Tafel slope of 241 mV/dec, and stable amperometric response for 5 h duration with slight drop of 19 mV overpotential.

The electrode materials which have been investigated as part of this present study, showed a versatile electrochemical behavior. Supercapacitor electrode with high voltage window and enhanced energy storage ability were demonstrated. Alkaline HER measurements on the samples exhibited high stability, low overpotential and high catalytic stability. Alkaline OER experiment on MFO-1 revealed a high overpotential which can be attributed to high binding energy of hydroxide intermediaries with the catalytic surface and low surface coverage. We found good OER stability response indicating the robust nature of MFO-1 in electrocatalyst role. The electrode materials used in our study can be synthesized very cheaply and are non-toxic in nature, which increases its potential in green energy stororage role.

Keywords: supercapacitors, energy density, voltage window, electrocatalyst, overpotential, catalytic stability