Electrochemical investigations on polymer based ternary nanocomposites, exfoliated MAX phase (Ti_3AlC_2) and lithium iron phosphate

A thesis submitted in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

Ms. Devalina Sarmah

Registration Number: TZ121548 of 2012

Department of Physics

School of Sciences

Tezpur University

Napaam, Sonitpur-784028

Assam, India

November, 2022

Conclusion and future prospects

7.1 Conclusion

This chapter outlines the main conclusion drawn from the thesis. The thesis work could be divided into two parts (Part A and Part B). Part A (Chapter 2-4) illustrates facile synthesis methods and electrochemical investigations on ternary nanocomposites of molybdenum disulphide, reduced graphene oxides and conducting polymers such as poly(3,4-ethylenedioxythiophene) and polypyrrole for supercapacitor applications. Polypyrrole based ternary nanocomposite electrode was modified with 100 MeV O^{7+} swift heavy ions (SHI) irradiation to tune the physico-chemical and electrochemical properties. Part B (Chapter 5, 6) discusses the complex Al^{3+}-ion electrochemistry of exfoliated MAX phase (Ti_3AlC_2) and $LiFePO_4$ exclusively in aqueous electrolyte. The chapter-wise significant findings of the thesis are outlined as follows:

Chapter 2: Ternary nanocomposite of molybdenum disulfide, reduced graphene oxide and poly(3,4-ethylenedioxythiophene) for supercapacitor

1. The common problem associated with rGO nanosheets is agglomeration which reduces the total available surface area during electrochemical processes. To mitigate this issue, MoS_2-rGO layer-by-layer structure was fabricated by one-step self-assembly method. MoS_2-rGO layer-by-layer structure effectively averts the agglomeration of rGO nanosheets as well as prevents the restacking of MoS_2 nanosheets.
2. Fabrication of electrode material with stable cycling performance, enhanced surface area and improved electrode/electrolyte interactions is expected in order to reach supercapacitor goals. Ternary Mo_{S2}-rGO/PEDOTNPs nanocomposite was synthesized with PEDOTNPs and MoS_2-rGO layer-by-layer structures exploiting a hydrothermal reduction process. PEDOTNPs, MoS_2/PEDOTNPs and rGO/PEDOTNPs nanocomposites were also synthesized for comparison.
3. Mesoporous and hydrophilic ternary MoS_2-rGO/PEDOTNPs electrode exhibits specific capacitance of 1143.7 Fg^{-1} at 1 Ag^{-1} of current density. The

ternary electrode retains 73.3% (840 Fg^{-1}) of capacitance at 9 Ag^{-1} of current density and 97.7% of cycle life after repeated 3000 charge/discharge cycles.

4. The charge storage process is the combination of diffusion controlled faradic process and non-diffusive capacitive process for ternary MoS_2-rGO/PEDOTNPs electrode. Overall, capacitive controlled contribution is 27.5% at the scan rate of 5 mVs^{-1} for the ternary MoS_2-rGO/PEDOTNPs electrode.
5. Further, electrochemical performance of MoS_2-rGO/PEDOTNPs//MoS_2-rGO/PEDOTNPs symmetric supercapacitors was investigated to understand the applicability in practical applications. Symmetric supercapacitor of MoS_2-rGO/PEDOTNPs//MoS_2-rGO/PEDOTNPs exhibits specific capacitance of 289.25 Fg^{-1} at 1 Ag^{-1} of current density and 93% of cycling stability after 10,000 repeated charge/discharge cycles at 20 Ag^{-1} of current density. A maximum specific energy of 33.56 $Whkg^{-1}$ could be achieved with specific power of 450 Wkg^{-1} by the supercapacitor at 1 Ag^{-1} of current density.

Chapter 3: Layer-by-layer self-assembly of MoS_2, rGO and polypyrrole nanotubes for enhanced electrochemical performance of supercapacitor

1. Ternary MoS_2-rGO/PPyNTs nanocomposite was synthesized by dispersing pre-synthesized polypyrrole nanotubes (PPyNTs) in MoS_2-GO layer-by-layer structures followed by *in-situ* hydrothermal reduction of GO. MoS_2-PPyNTs, rGO-PPyNTs and PPyNTs electrodes were also prepared to compare the electrochemical performance of the ternary electrode.
2. MoS_2-rGO/PPyNTs ternary nanocomposite delivers enhance specific capacitance of 1561.25 Fg^{-1} at the current density of 1 Ag^{-1} and specific capacitance of 1145.2 Fg^{-1} at 6 Ag^{-1} exhibiting an excellent rate performance.
3. MoS_2-rGO/PPyNTs ternary electrode possesses cycling stability of 72% of initial specific capacitance after 10,000 cycles at 10 Ag^{-1} of current density which is comparatively low for supercapacitor electrodes in neutral aqueous electrolyte. Morphology of the ternary electrodes before and after cycling discloses swelling and shrinkage in PPyNTs. Swelling and shrinkage in PPyNTs are the reasons behind low specific capacitance of the ternary electrode after cycling.

4. MoS_2-rGO/PPyNTs // MoS_2-rGO/PPyNTs symmetric supercapacitor delivers specific capacitance of 330 Fg^{-1} at 1 Ag^{-1} of current density and retains only 53% of cycling stability after 5000 repeated GCD cycles.

Chapter 4: Electrochemical study on ion beam modified ternary composite of molybdenum disulfide, -reduced graphene oxide and / polypyrrole nanotubes

1. Surface modification of 2-D reduced graphene oxide (rGO), molybdenum disulfide (MoS_2) nanosheets and conducting polymer such as polypyrrole nanotubes (PPyNTs) is worth exploring for the application of electrochemical supercapacitors.
2. Swift heavy ion (SHI) irradiation is a controlled surface modification tool that significantly modifies various properties of electrode material at electronic and molecular level. Conducting polymers are irradiation sensitive and many of the physico-chemical properties can be altered with SHI irradiation. MoS_2 and reduced graphene oxide (rGO) are also SHI irradiation sensitive.
3. The ternary MoS_2-rGO/PPyNTs nanocomposite was irradiated with 100 MeV O^{7+} swift heavy ions (SHI) at four different fluences of $3.3x10^{11}$, $1x10^{12}$, $3.3x10^{12}$ and $1x10^{13}$ ions cm^{-2}. From, morphological characterization (FESEM), it was observed that structural defects like folding and incision appear in the electrode at a fluence of $3.3x10^{12}$ ions cm^{-2}.
4. Upon SHI irradiation, the electrochemical properties such as specific capacitance, cycling stability, rate capability and Coulombic efficiency were improved up to a fluence $3.3x10^{12}$ ions cm^{-2} and degraded at the highest fluence of 10^{13} ions cm^{-2}.
5. An enhancement in the specific capacitance could be observed for SHI irradiated nanocomposite. The capacitance value is 1875 Fg^{-1}, whereas the pristine electrode shows a capacitance of ~ 1561 Fg^{-1}. Such an improvement is attributed to the change in crystallinity, electro-active surface area and electrode kinetics upon SHI irradiation.
6. The irradiated nanocomposites demonstrated good cycling stability (91% retention after 10,000 galvanostatic cycles) than that of the pristine electrodes (70% cycling stability). It is due to the enhanced stability of the oxidation

states of PPyNTs from the increased $\pi - \pi$ interaction in the polymer chain after SHI irradiation.

Chapter 5: Electrochemical exfoliation of Ti_3AlC_2 MAX phase and unusual Al^{3+} ion storage in aqueous electrolyte

1. The processing of MXenes in general involves steps which raise safety concerns. A vast majority of MXenes are processed using HF acid because it can selectively etch the A elements (mostly group 13 and 14 elements of the periodic table) present in the MAX phase. It is well-know that HF acid is extremely reactive and it can cause serious and, at times, fatal injuries when comes in contact with human skin. Therefore, stringent and specialized procedures are always followed while handling HF acid to maintain safety. Electrochemical etching technique may be a novel choice in this context.
2. Effective exfoliation could be achieved for MAX phase (Ti_3AlC_2) when a hybrid aqueous electrolyte is utilized for the electrochemical treatment. The electrolyte is an aqueous mixture of $AlCl_3$ and NaOH (1:10 v/v).
3. The electrochemically exfoliated MAX phase shows unusual diffusion-controlled Al^{3+}-ion storage behavior in aqueous electrolyte. Such Al^{3+} ion storage behavior for MAX phase (Ti_3AlC_2) was not seen earlier.

Chapter 6: Al^{3+} ion storage behavior of $LiFePO_4$ in aqueous electrolyte

1. $LiFePO_4$ is considered as an important cathode material for lithium-ion batteries due to the possibility of replacement of toxic and scare cobalt with environment friendly and abundant iron species.
2. $LiFePO_4$ was extensively investigated in non-aqueous electrolyte and only handful of reports on the aqueous Li^+-ion electrochemistry of $LiFePO_4$ for rechargeable aqueous batteries is available.
3. The chapter illustrates the electrochemical behaviour of $LiFePO_4$ in Al^{3+}-ion conducting aqueous electrolyte for the first time. It is inferred from the electrochemical measurements that Al^{3+}-ion together with the structural Li^+-ion could take part in the reversible oxidation-reduction process of $LiFePO_4$.
4. It is also found that leaching of iron species from $LiFePO_4$ in the electrolyte results in low cycling stability. This could be mitigated to an appreciable

degree by tweaking the electrolyte composition with a low fraction of iron species in the electrolyte. In this context, addition of iron chloride in the electrolyte could stabilize the cycling profiles by almost 23.5 %.

7.2 Future outlook

The thesis work concentrates on conducting polymer based ternary electrodes for supercapacitor applications and suitable electrode materials for Al^{3+}-ion storage. Some of the future prospects of the thesis are as below:

1. Different types of conducting polymer based hybrid nanocomposites with carbon nanotubes, MXenes, metal oxides, metal sulphate etc. may be investigated for electrochemical supercapacitors and Al^{3+}-ion storage.
2. Tuning the properties of electrode materials with plasma irradiation, low energy ion irradiations is also a novel idea and further the changes in electrochemical properties can be studied.
3. Carbon coating or doping in $LiFePO_4$ is expected to result in better cycle life in Al^{3+}-ion based electrolytes as was shown for Li^{+}-ion systems.
4. Identification of new electrodes and electrolytes for efficient Al^{3+}-ion storage.