Graphene-based energy storage materials for supercapacitor application

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By

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CHAPTER 6

Summary & future perspectives

In the current research, focus has been given on synthesizing ternary composites for supercapacitor electrodes. Various electrochemical parameters like specific capacitance, coulombic efficiency, specific energy, specific power, cycle life, charge transfer resistance, etc. have been considered while fabricating supercapacitors. There are few kinds of research that suggest that composites exhibit high charge transfer resistance as well as low specific energy and power than the individual components due to pore blockage. There are a few types of research as well where composites exhibit outstanding electrochemical properties than the individual components due to the contribution of the participating compounds. The most suitable sub-class of graphene is graphene oxide due to the presence of various types of active functional groups like carboxyl, hydroxyl, and carbonyl. Polyaniline is chosen over other conducting polymers because of its outstanding redox activities. The use of graphene oxide fulfilled a dual purpose, i.e., the role of carbon-based material as well as a conductive filler. Less research has been done on AB_2O_4 (A and B are metals, and O stands for oxygen) type metal oxides. So, we prepared $CuCo_2O_4$, $CuFe_2O_4$, and $CoFe_2O_4$ and checked their electrochemical properties.

We have successfully synthesized GO using the modified hummers method for supercapacitor electrode applications. GO exhibited the highest value of specific capacitance, specific energy, and specific power of 153.41 F/g, 8.77 Wh/kg, and 300.01 W/kg, respectively. It offers a very low charge transfer resistance of 19.76 Ω during the electrochemical processes and 92.04 % capacitance retention after 5000 cycles. The robust electrochemical behavior could be due to the uniform sheet like morphology of the corresponding system, which might be providing seamless movement of the electrolyte ions to the electrochemically active sites along with proper electrical connection.

Three types of ternary composite systems based on graphene oxide-polyaniline-bimetallic oxide was synthesized. We comparing the electrochemical properties of the ternary systems with their single graphene oxide and binary systems, it was found that ternary systems exhibited superior electrochemical properties than their counterparts.

Graphene oxide-polyaniline-copper cobaltite (GO/PANI/$CuCo_2O_4$) based symmetric two-electrode system exhibited a specific capacitance of 312.72 F/g at 1 A/g. It had the specific energy, specific power, and capacitance retention of 62.54 Wh/kg, 300.04 W/kg, and 84.25 %, respectively. The specific energy decreased to 46.73 Wh/kg and 41.76 Wh/kg at 10 A/g and 20 A/g, respectively. The system exhibited a specific power of 5997.61 W/kg at 20 A/g. It had a charge transfer resistance of 12.23 Ω and a response time of 632.91 ms.

Graphene oxide-polyaniline-copper ferrite (GO/PANI/$CuFe_2O_4$) based symmetric two-electrode system exhibited a specific capacitance of 357.28 F/g at 1 A/g. It had the specific energy, specific power, and capacitance retention of 71.45 Wh/kg, 300.03 W/kg, and 78.77 %, respectively. The specific energy decreased to 47.72 Wh/kg and 42.85 Wh/kg at 10 A/g and 20 A/g, respectively. The system exhibited a specific power of 5983.90 W/kg at 20 A/g. It had a charge transfer resistance of 8.72 Ω and a response time of 158.73 ms.

Graphene oxide-polyaniline-cobalt ferrite (GO/PANI/$CoFe_2O_4$) based symmetric two-electrode system exhibited a specific capacitance of 346.92 F/g at 1 A/g. It had the specific energy, specific power, and capacitance retention of 69.38 Wh/kg, 300.08 W/kg, and 79.03 %, respectively. The specific energy decreased to 46.02 Wh/kg and 40.82 Wh/kg at 10 A/g and 20 A/g, respectively. The system exhibited a specific power of 5989.37 W/kg at 20 A/g. It had a charge transfer resistance of 8.51 Ω and a response time of 316.45 ms.

It was observed that the specific capacitance and the specific energy decreased with the increase in scan rate and current. At higher scan rates and current, electrolyte ions do not get enough time to complete the desirable redox transitions and the system becomes sluggish. Hence reduced values of specific capacitance and energy are obtained.

In all three optimized ternary composites, the equivalent electrical circuit is consisting of capacitive elements, constant phase elements, and resistive elements. The capacitive elements can be assigned to capacitance due to EDLC, pseudocapacitive, and mass capacitance. EDLC was due to the presence of graphene oxide in the composite. Pseudocapacitance must be coming from polyaniline and binary metal oxides. The low-frequency straight line represents mass capacitance, an ideal polarizable capacitance. The slope of this line indicates that a resistance known as leakage resistance is connected to the mass capacitance. The current collector, substrate, electrolyte, substrate, and active material contact resistance, as well as Warburg resistance (due to diffusion resistance), must be the sources of the additional resistances. The low-frequency graphs are not parallel to the z-imaginary axis, which causes all of the systems to deviate from the ideal capacitor behavior. Q has been added as a constant phase element to the equivalent circuit.

Due to the presence of redox transitions at the electrode surface, conducting polymers and transition metal oxides have greater energy density and specific capacitance. The poor inherent conductivity of metal oxides causes them to have poor cycle stability and poor rate capability. The objective of the graphene oxide was to provide sufficient surface area to the electroactive components (in this case, bimetallic oxides and polyaniline) and to maintain the structural integrity of metal oxides and polyaniline by withstanding mechanical distortion during redox transitions.

Future perspectives

Specific energy and power play a significant significance in energy storage systems. Similarly, a supercapacitor's integral properties include high specific capacitance retention and low charge transfer resistance. To broaden the stability potential window and decrease the systems' charge transfer resistances, a variety of electrolytes with various molarities can be used. This will improve both the specific power and the specific energy because they are closely related to the potential window (directly proportional to the specific energy). The electrochemical impedance spectroscopy (EIS) data can be validated by simulation using COMSOL in the situation of electrical double-layer capacitance. But when it comes to composites, where the pseudocapacitive nature predominates, it is particularly challenging. Finding the contributions from different systems by simulating the EIS data of ternary composites may be extremely beneficial. In general, materials that are used in batteries have a high energy density, while materials used in supercapacitors have a high power density and a long cycle life. If we combine both types of materials into one system, the system will have a higher specific energy output, more power, and a longer operational life. If artificial intelligence and machine learning are incorporated into the next studies in this subject, it may be possible to greatly reduce the amount of work required and increase production with greater precision.