

Importance and control of surface properties of carbon materials in energy storage and conversion systems-II

For carbon-based double-layer capacitors, the presence of surface groups is known to influence the electrochemical interfacial state of the carbon surface and its double-layer properties that include: wettability, point of zero charge, electrical contact resistance, adsorption of ions (capacitance), and self-discharge characteristics. Graphitic carbon surfaces can be regarded as being made up of (at least) two chemically different kinds of sites: basal and edge carbon sites. Edge sites are considered to be more reactive than basal sites as they are often associated with unpaired electrons. This view is supported by the observation that the reactivity of edge sites towards oxygen, for high purity graphite, is an order of magnitude greater than that of basal sites. Consequently, the chemical properties of carbons also vary with the relative fraction of edge sites and basal plane sites; with the ratio of edge to basal sites generally increasing with the degree of disorder. Functional groups that are electrochemically inert in the potential range of operation of the device can enhance the wettability of carbon electrodes and, consequently, increase the specific capacitance of the carbon through improved pore access and greater surface utilization.

Porous carbons are almost invariably associated with appreciable concentrations of heteroatoms, which are primarily oxygen and hydrogen, and to a lesser degree, nitrogen, sulfur and halogens. These heteroatoms are derived from the starting materials and become part of the chemical structure as a result of incomplete carbonization. They may also be incorporated on to the carbon surface during subsequent treatment or exposure to air. Carbons can readily physisorb (i.e., reversible adsorption) molecular oxygen upon exposure to air, even at sub-ambient temperatures. Oxygen chemisorption (irreversible adsorption) also begins to occur at low temperatures and increases with temperature to form various oxygen-based functionalities on the carbon surface. Carbon–oxygen complexes are by far the most important surface group on carbons. Three types of surface oxides, namely, acidic,

basic and neutral, have been proposed to form on carbon surfaces as determined by the formation history of the carbon material and the temperature at which it was first exposed to oxygen. Acidic surface oxides are formed when carbons are exposed to oxygen between 200 and 800°C or by reactions with oxidizing solutions at room temperature. These surface groups are considered to be less stable and include groups such as carboxylic, lactonic and phenolic functionalities. Basic and neutral surface oxides are considered to be more stable than acidic oxides and tend to form after a carbon surface, freed from all surface compounds by heat treatment, comes in contact with oxygen at low temperatures.

The extent of oxygen retention as physically adsorbed molecular oxygen, or as surface complexes, is believed to influence strongly the rate and mechanism of capacitor self-discharge. In particular, carbons with a high concentration of acidic surface functionalities are prone to exhibit high rates of self-discharge. The increase in leakage current suggests that the oxygen functional groups may serve as active sites, which can catalyse the electrochemical oxidation or reduction of the carbon, or the decomposition of the electrolyte components. Conversely, the removal of oxygenated surface functionalities by high-temperature treatment in an inert environment results in lower leakage currents. The presence of oxygenated functional groups can also contribute to capacitor instability, which results in an increased resistance and deterioration of capacitance. The removal of oxygen from the carbons used in supercapacitor electrodes generally improves their stability.

Oxygen surface functional groups have also been shown to influence the rest potential of activated carbons. The rest potential of activated carbons was found to be proportional to the logarithm of the oxygen content or to the concentration of acidic surface sites. Carbons with a high rest potential will experience undesirably higher voltages when charged and this could lead to gas generation. Whilst charge storage on carbon electrodes is predominantly capacitive, there are also contributions from surface functional groups that can be rapidly charged and discharged and give rise to pseudocapacitance.

Various oxidative treatments have been applied to carbons, but it is often difficult to isolate the chemical changes from the physical and structural changes that frequently accompany oxidative treatments. Hsieh and Teng used a relatively mild oxidative technique to oxidize polyacrylonitrile-activated carbon fabrics without introducing significant physical changes to the carbon. It was found that the Faradaic current, a direct measure of pseudocapacitance, increased significantly with the extent of oxygen treatment, while the change in double-layer capacitance was only minor. The large increase in specific capacitance (from ~120 to 150 F g⁻¹) was, however, accompanied by undesirable increases in internal resistance and leakage current.

References

1. *Journal of Power Sources* 157 (2006) 11–27
2. C.-T. Hsieh, H. Teng, *Carbon* 40 (2002) 667.