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

Surface area, pore size and size distribution play important roles in the porous electrodes suitable for battery, fuel cell and supercapacitor applications. The most significant impact for the porosity of a porous electrode is on the kinetics for ionic diffusion within the matrix. Porosity is one of the most important engineering factors for the design or the porous electrodes. According to IUPAC classification, pore size can be classified in three categories: micropores with width less than 2 nm; mesopores with width between 2 and 50 nm and macropores with width larger than 50 nm. Figure 1 illustrates the micro, meso and macropores in a porous electrode material particle.

The surface area of a porous material is the sum of the surface area contributed from all the pores. In general, the porosity of a given mass of solid material is related to the size of the constituent particles. In practice, the particles of a fine powder, the primary particles, will stick together due to the surface force to form secondary particles. Pores not only locate within the aggregated particles, in which the pore size depends on the size and shape of primary particles and how they are packed together, but also remain within the primary particles themselves for which the pore size is determined by the raw material and the production process of the electrode material.
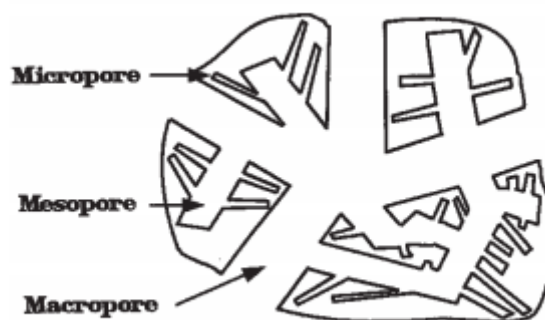

Figure 1. Pores in a porous electrode material particle

Micropores are interconnected by themselves as part of the microporous system. The contact between primary particles is believed to be Van der Vass force. Mesopores are formed

in those aggregated primary particles. When a porous electrode is dipped into electrolyte, interconnections of mesopores and micropores not only provide the sites for electrolyte to reside, but also provide the pathway for the ionic diffusion. Thus, the network of the porosity of the porous material determines the kinetics of ionic diffusion.

While activated carbons, particularly those derived from naturally occurring precursors, tend to contain pores from all three-size classes, careful selection of the carbon precursor and the activation conditions does allow significant control over the relative contribution of each size class. Materials with the highest surface-area are consistently obtained from highly microporous activated carbons, with high pore volumes, in which >90% of the total pore volume arises from microporosity.

While the vast majority of open pores can contribute to the measured surface-area, not all pores are electrochemically accessible. Ultimately, pore sizes will approach the double-layer dimensions, with the result that the movement of electrolyte will be restricted and, eventually, there will be a limitation on the ability of the electrolyte to form a double-layer. The surface-area arising from pores in this size range (which are dependent on electrolyte molecular dimensions) would not be effectively utilized and is unlikely to contribute to performance of the electrode.

It is critical to understand the distribution characteristics of a porous electrode. Thus, the kinetics of electrochemical accessibility depends on the electrode surface area, which in turn depends on the pores of various sizes. In order to engineer the porous electrodes for the applications of various power and energy demands, it has to be taken into account that not all the pores in the matrix of a porous electrode are available to be accessed electrochemically at the same time. Therefore, "electrochemical accessible" surface area becomes more critical to the engineering of a porous electrode than the physical surface area. The electrochemical porosimetry based on impedance experimental technique and transmission line modeling (TLM-PSD) is the technique which is directly related to the measurements of "electrochemical accessible" surface area or porosity. The electric conductivity or the ohmic resistance of porous materials is closely related to their morphologies. Generally, the higher the surface area, the smaller the particle size, and the poorer the conductivity should be. The optimal pore size depends on the ion size and operating voltage of the device. Narrowing the pore size distribution (PSD) leads to an increase in the stored energy density. This means porous electrode with a carefully selected pore size, would be ideal for the energy storage of nano-porous supercapacitors.

Besides the kinetic factors related to the pore size distribution, electric conductivity is another limiting factor for the power density. It is worth distinguishing the electric conductivity of the electrode material e.g. porous carbon, which is in the solid side of electrode from the ionic conductivity, which relates to the mobility of ions in the liquid side. Establishing double-layer on the surface of a porous electrode includes separation of ions with opposite charges and the movement of ions to opposite direction inside the pores of porous material. The mobility of the ions inside the porous matrix is responsible for the rate of electrochemical accessibility. Obviously, the movement of the ions in smaller pores is more difficult than in larger pores. So, the ionic conductivity inside the matrix of the porous material is conceptually different with that in the bulk of electrolyte.

References

1. *Journal of Power Sources 157 (2006) 11–27.*
2. *Energy Environ. Sci., 2012, 5, 6474–6479*
3. *AIP Conference Proceedings 1597, 14 (2014); https://doi.org/10.1063/1.4878477*