

Acknowledgment

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About the Author

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The 2007 Colin Garfield Fink Summer Research Fellowship — Summary Report

Fabrication, Structure, and Electrochemistry of Iodated Microporous Carbons of Low Mesoporosity

by Prabeer Barpanda

Electrochemical double layer capacitors (EDLCs), often known as supercapacitors, are increasingly popular in various energy storage applications ranging from consumer electronics to hybrid electric vehicles.^{1,2} EDLCs employ high surface area, mesoporous activated carbons, in which charge storage is primarily due to the formation of electrostatic non-Faradaic double layer reaction and interfacial charge separation. In recent years, there has been ongoing and successful effort to produce high capacity carbon electrodes by careful tuning of the meso- and micro-porosity of the carbons. We have recently focused on the improvement of the volumetric capacity of such carbons for intermediate time constant applications. In an alternative approach, we have reported significant rise (200-500%) in volumetric capacity of activated carbons by iodine modification.^{3,4} We have shown iodination of activated carbon indicates the formation of carbon-polyhalide compounds due to charge transfer (CT) reaction,

thereby altering the existing physical and electrochemical properties of carbon in the non-Faradaic development of reversible Faradaic reaction. The polyiodides were preferentially located in the micropores. The focus of this work is to study the fabrication, validation and physico/electrochemical properties of a microporous carbon from low cost precursors.

Microporous carbon (IUPAC definition: 0-2 nm) was prepared from coal following chemical activation method.⁵ Anthracite coal was grounded and mixed with KOH solution in water at 60°C for 2 h. The solution was dried overnight at 110°C. The resulting slurry was taken in an alumina crucible and was annealed at 750°C for 1 h for activation in nitrogen atmosphere. The annealed powder was mixed with HCl solution to neutralize the existing KOH. Upon drying the powder overnight, pure microporous carbon was successfully obtained.

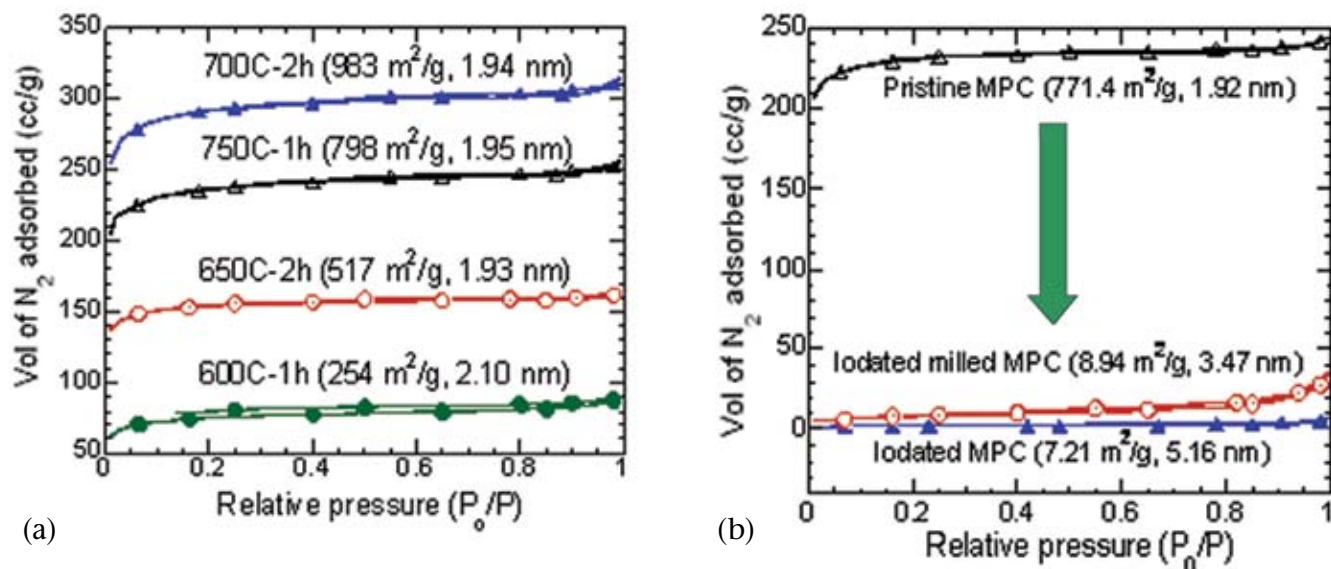


FIG. 1. (a) The BET isotherms of microporous carbons produced at different activation condition (annealing temperature and soaking time). They resemble the IUPAC type-I pattern proving the presence of only microporosity. (b) The BET isotherms showing the drastic decrease in N₂ adsorption isotherm upon iodination (as shown by arrow) indicating the filling of micropores with iodine particles. (The numbers in brackets indicate surface area and average pore size respectively.)

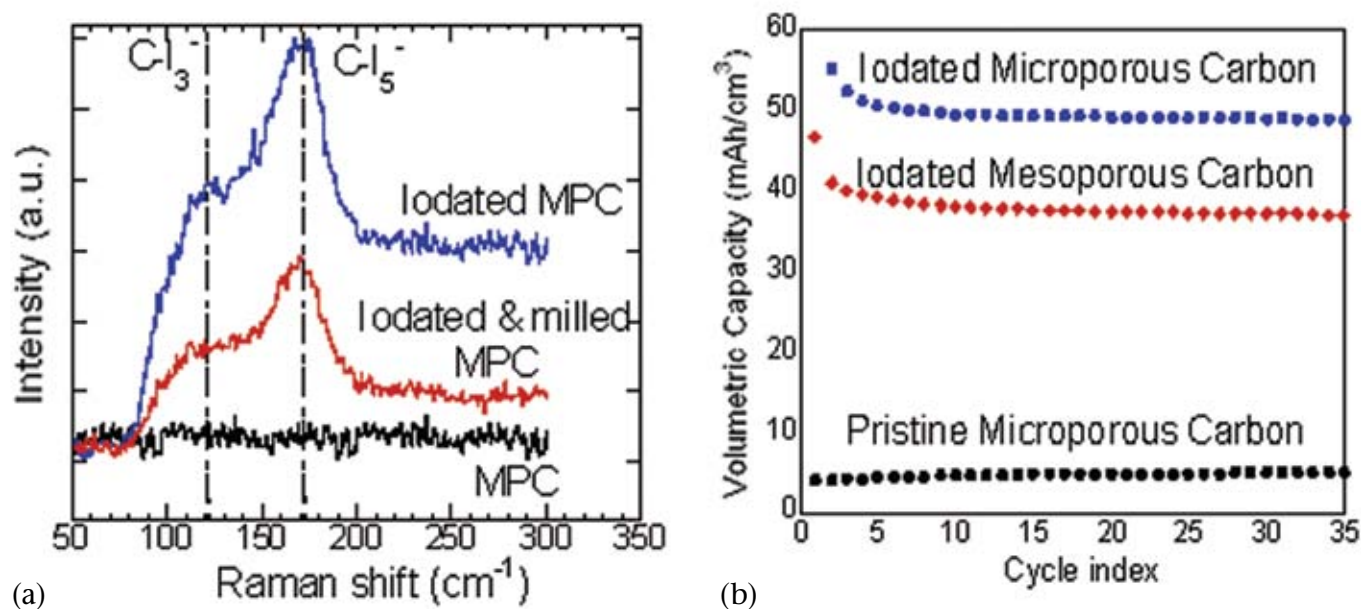


Fig. 2. (a) Raman spectra showing the formation of polyiodides (i.e. C-I₃- and C-I₅-) upon iodation of microporous carbon. (b) A representative graph showing the notable increase in electrochemical capacity of microporous carbon upon incorporation of iodine.

Depending on the annealing temperature and soaking time, the surface area and microporosity can be controlled. Figure 1a shows the BET nitrogen adsorption isotherms of representative microporous carbons prepared at 600–800°C for 1–2 h. These isotherms match well with an IUPAC type-I isotherm confirming the presence of 100% microporosity. These microporous carbon show relatively high surface area (600–800 m²/g) coupled with micropores of average size 1.95 nm. Later, the in-house prepared microporous carbons were halidated with different amount of iodine (20–40 weight %) by a vapor iodation treatment at 170°C for 2 h.⁴ These iodated carbons were morphologically modified by milling for 20 minutes, which introduces some mesoporosity while retaining majority of micropores. The BET isotherm shown in Fig. 1b shows a significant reduction of micropore volume suggesting the iodine products are present within the microporosity.

The induction of iodine into the carbon matrix results in the formation of carbon-iodine nanocomposites with significant change in its physico-electrochemical properties. Iodine, being a weak electron acceptor, can induce a charge transfer reaction with carbon. This charge transfer reaction instigates the formation of various carbon-polyiodide compounds. Raman spectroscopy of these iodated microporous carbons demonstrates the presence of C-I₃⁻ and C-I₅⁻ compounds (Fig. 2a). This in turn modifies the electronic and electrochemical behavior of pristine carbons. The galvanostatic study reveals (i) increase in non-Faradaic capacity and (ii) the appearance of a Faradaic plateau (at 3.1 V). Collectively, the electrochemical and volumetric capacity of iodated microporous carbon increases significantly as shown in Fig. 2b. These iodated microporous carbons have higher volumetric capacity than that of any mesoporous activated carbons.

A detailed study comprising the synthesis, physico-chemical, structural, morphological, and electrochemical study of this new class of iodated microporous carbons will be reported soon. Although in its infancy, such a hybrid approach may offer interesting insights into future electrode materials for hybrid supercapacitors and high power batteries.

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