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The Graphene/Oxidized MWCNT Supercapacitor Incorporated with Ionic Liquid Electrolyte

Recently, there is more and more attention to be paid to improve the energy density of carbon-based electrode supercapacitors. Graphene, as a kind of two-dimensional material, is promising in the application of electrochemical capacitors (EDLC) due to its unique properties such as high specific surface area (SSA), excellent electrical conductivity, good chemical stability and outstanding mechanical behavior. It has been recognized that the specific capacitance of graphene materials could be further enlarged by preventing the re-stacking phenomenon of graphene layers [1]. A common method carried out is adding spacers and carbon nanotubes (CNTs) have been demonstrated as an effective one. However, some problems still limit the enhancement of energy density. One is the lack of linearity between the capacitance and specific surface area. In other words, the larger specific surface area sometimes doesn't lead to larger specific capacitance. The specific capacitance is proportional to the specific surface area of accessible pores rather than that of total pores. Besides, the specific capacitance provided by accessible pores could be different in pores with structures. It depends on the different ionic behaviors in different pores. In order to realize the desired performance, it is of great importance to clarify the pore structures of electrode materials and its relationship with ionic behaviors, which is directly related to the process of charge storage and the capacitance. To address this issue, graphene/CNT composite with different pore structures is synthesized by adjusting the ratio of the spacer in the material, where chemical reduction is utilized [2]. The pores in the range of ion size and solvated size could contribute the most to specific capacitance in aqueous or organic electrolytes. The additional capacitance in this type of pores is suggested to be due to the desolvation of ions [3]. Unfortunately, this conclusion is difficult to be applied in supercapacitors based on ionic liquid since no solvent is used in this kind of electrolyte. Namely, ions are not solvated at all in ionic liquids. Thus, the electrochemical performance is based on the form of coin cell where the reduced oxidized MWNT/GO composites as electrode materials and a kind of ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF$_4$), as the electrolyte. The pores are classified into three types according to the ratio of pore size to ion size in ionic liquids (Figure 1). And the relationship between pore structure and specific capacitance in an ionic liquid is analyzed by linear fitting methods. The results of analysis indicate that pores with radii in the range of two to three times of cation and anion-pairs are the most efficient pores for both cations and anion-pairs. It is due to the changed ion packing configuration in different pores, which is related to the stronger ion-ion correlation in ionic liquids. In addition, pores smaller than the ion sizes could hinder the utilization of larger pores when the ink-bottle structure is present. Considering the larger size of EMI$^+$ (0.43 × 0.76 nm) than BF$_4^-$ (0.48 × 0.48 nm), we have preferred the size of EMI$^+$ as the standard to classify the pores. It is found that pores with radius larger than 0.76nm, namely twice the size of ions, can make greater contributions to the specific capacitance (Figure 2).

References

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[2] W.S. Hummers, R.E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339–1339
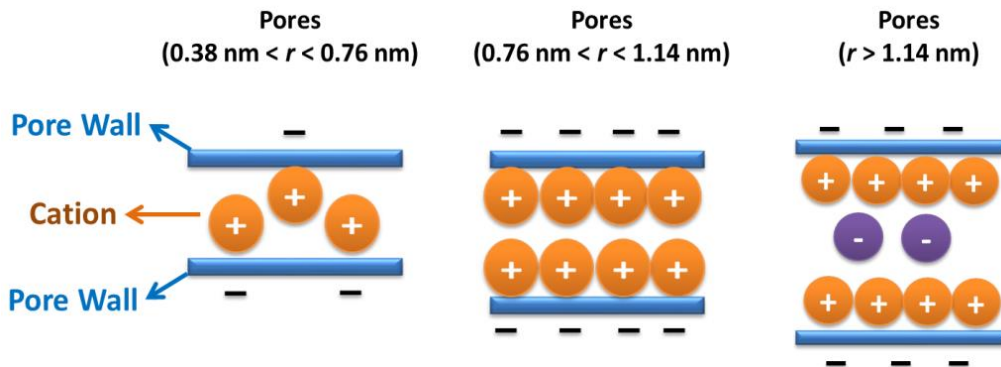[3] Li Jing, Tang Jie , Yuan Jinshi et al, Chemical Physics Letters, 693 (2017) 60-65

Figures

Figure 1: Schematic explaining effects of ion configuration on capacitance in different pores
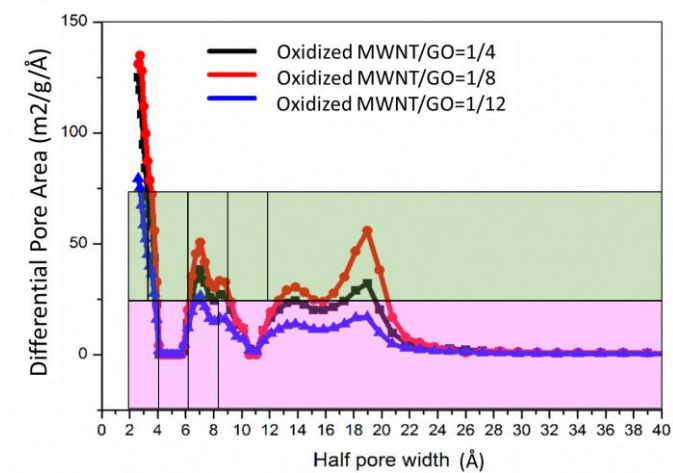

Figure 2: Schematic diagram of the pore distribution and the differential pore area for different MWNT addition