

Lithium and Sodium Ion Capacitors with High Energy and Power Densities based on Carbons from Recycled Olive Pits

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Abstract : Hybrid capacitor configurations are now of increasing interest to overcome the current energy limitations of supercapacitors entirely based on non-Faradaic charge storage. Among them, Li-ion capacitors including a negative battery-type lithium intercalation electrode and a positive capacitor-type electrode have achieved tremendous progress and have gone up to commercialization. Inexpensive electrode materials from renewable sources have recently received increased attention since cost is a persistently major criterion to make supercapacitors a more viable energy solution, with electrode materials being a major contributor to supercapacitor cost. Additionally, Na-ion battery chemistries are currently under development as less expensive and accessible alternative to Li-ion based battery electrodes. In this work, we are presenting both lithium and sodium ion capacitor (LIC & NIC) entirely based on electrodes prepared from carbon materials derived from recycled olive pits. Yearly, around 1 million ton of olive pit waste is generated worldwide, of which a third originates in the Spanish olive oil industry. On the one hand, olive pits were pyrolyzed at different temperatures to obtain a low specific surface area semigraphitic hard carbon to be used as the Li/Na ion intercalation (battery-type) negative electrode. The best hard carbon delivers a total capacity of 270mAh/g vs Na/Na+ in 1M NaPF₆ and 350mAh/g vs Li/Li+ in 1M LiPF₆. On the other hand, the same hard carbon is chemically activated with KOH to obtain high specific surface area -about 2000 m²g⁻¹- activated carbon that is further used as the ion-adsorption (capacitor-type) positive electrode. In a voltage window of 1.5-4.2V, activated carbon delivers a specific capacity of 80 mAh/g vs. Na/Na+ and 95 mAh/g vs. Li/Li+ at 0.1A /g. Both electrodes were assembled in the same hybrid cell to build a LIC/NIC. For comparison purposes, a symmetric EDLC supercapacitor cell using the same activated carbon in 1.5M Et₄NBF₄ electrolyte was also built. Both LIC & NIC demonstrates considerable improvements in the energy density over its EDLC counterpart, delivering a maximum energy density of 110Wh/Kg at a power density of 30W/kg AM and a maximum power density of 6200W/Kg at an energy density of 27 Wh/Kg in the case of NIC and a maximum energy density of 110Wh/Kg at a power density of 30W/kg and a maximum power density of 18000W/Kg at an energy density of 22 Wh/Kg in the case of LIC. In conclusion, our work demonstrates that the same biomass waste can be adapted to offer a hybrid capacitor/battery storage device overcoming the limited energy density of corresponding double layer capacitors.

Keywords : hybrid supercapacitor, Na-Ion capacitor, supercapacitor, Li-Ion capacitor, EDLC

Conference Title : ICSRD 2020 : International Conference on Scientific Research and Development

Conference Location : Chicago, United States

Conference Dates : December 12-13, 2020