Nanoporous pyropolymers containing numerous heteroatoms for amphicharge storage

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Nanoporous carbon-based electrode materials (CEMs) with high specific surface area are a strong candidate to achieve high electrochemical double layer (EDL) capacitance. At the same time, there is another surface-induced charge storage mechanism in CEMs besides the EDL mechanism, which sometimes surpasses the specific EDL capacitance.[1] Presence of oxygen groups plays a key role in the pseudocapacitive behaviors;[2] nitrogen atoms doped into a hexagonal carbon structure (by substituting for carbon atoms) can also enhance specific capacity by improving electrical conductivity with electron doping.[3] It was reported that heteroatom pairs, such as oxygen and nitrogen, on the edge site of the hexagonal carbon structures could store Li-ions in the cathodic voltage region through their synergistic behaviors,[3] indicating that the introduction of more heteroatoms on the edge sites could result in more charge being stored. In contrast, heteroatoms on the basal plane of the hexagonal carbon structures could break the conjugated carbon bonding, deteriorating electrical conductivities of the hexagonal carbon structures. In addition, intrinsic edge defects and pseudo-edge sites of hexagonal carbon structures are possible redox hosts.[4] Hence, the carbon textural properties and heteroatoms configurations have a key role in the pseudocapacitive charge storage. If these redox-active sites are exposed and in direct contact with an electrolyte, no solid state ion diffusion is required for a Faradaic reaction, and high energy and high power characteristics result. Therefore, hierarchical nanoporous carbon-based structures, composed of multimodal nanopores and numerous surface heteroatoms, can be an optimal architecture for surface-induced charge storage that is based on both redox reactions and EDL capacitance.

In this study, nanoporous pyropolymers (N-PPs) including numerous redox-active heteroatoms are fabricated from polyaniline nanotubes by heating with KOH. In the large operating voltage range 1.0–4.8 V versus Li^+/Li, N-PPs store amphicharges by a pseudocapacitive manner of Li-ion (mainly <3.0 V) and electrochemical double layer formation of anion (primarily >3.0 V). Through these surface-driven charge storage behaviors, N-PPs achieve a significantly high specific capacity of ~460 mA h g^{-1} at 0.5 A g^{-1}, maintaining specific capacities of 140 mA h g^{-1} at a high specific current of 30 A g^{-1} and 305 mA h g^{-1} after 2000 cycles at 3 A g^{-1}. Furthermore, asymmetric energy storage devices based on N-PPs deliver a high specific energy of 265 W h kg^{-1} and high specific power of 5081 W kg^{-1} with long-term cycling performance.

References:

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