ABSTRCT

Hard carbons are used as anode materials for lithium and sodium ion battery. Hard carbon gives better capacity than graphite for lithium ion battery and is the best anode option for sodium ion battery as graphite is unsuitable. Hard carbon comes in different sizes and nitrogen doping in hard carbon has given hope for further improvement. So to understand the effect of size and nitrogen doping in hard carbon as possible anode for lithium and sodium ion battery, experimental and theoretical studies have been done. For the experimental study, four varieties of carbon balls are synthesized of two different size ranges viz. micron and nano-sized. Two of these balls are nitrogen-doped, while the other two are un-doped. Nitrogen-doped nano-sized carbon (N-NCB) is synthesized using a unique one step hydrothermal method. We have demonstrated that the electrochemical performance of these hard carbon anode materials depends on the size. Nitrogen doping enhances the electrochemical performance of carbon balls and increases the active storage sites by enhancing the number of defects and porosity. For both the cases, LIBs and SIBs nitrogen doping show better improvement than nano sizing. For LIBs nitrogen doped micro balls (N-MCB) shows 8% improvement in capacity whereas nano carbon balls (NCB) shows 6.5 % improvement and N-NCB shows 14% improvement as comapared to micro carbon balls (MCB). The specific capacity of hard carbons for LIBs were 475, 506, 513 and 541 mAh/g for MCB, NCB, N-MCB and N-NCB, respectively. For SIBs N-MCB, NCB and N-NCB show capacity improvement of 30%, 19% and 39.5 % respectively compared to MCB. The specific capacity of hard carbonsfor SIBs were 205, 230, 266 and 286 mAh/g for MCB, NCB, N-MCB and N-NCB, respectively. Nitrogen doping also improves electrochemical performance by increasing electrical conductivity and controlling volume expansion. The density functional theory (DFT) study shows a significant reduction in volume expansion associated with lithiation and sodiation due to nitrogen doping. For LIBs volume expansion reduces by 60% whereas for SIBs it reduces by 44%. Also, the stress calculation shows a significant reduction of stress due to nitrogen doping for lithiation and sodiation. For nano balls, stress reduces by 88% and 80% for lithiation and sodiation after nitrogen doping. Whereas, for micro balls, nitrogen doping reduces stress by 82% and 66% for lithiation and sodiation. This increase in electrical conductivity, defects, porosity, reduction in volume expansion and stress in nitrogen-doped carbon samples makes them an excellent anode material for lithium and sodium ion batteries.

Keywords: Lithium-ion battery, Sodium-ion battery, Carbon anode, Volume expansion, DFT-simulation, radial stress, hoop stress