Polybenzimidazole Mediated N-Doping Along the Inner and Outer Surfaces of Carbon Nanofiber and Its Oxygen Reduction Properties

Beena K Balan a, Aiswarya Padinhare Manissey †a, Harshal D Chaudhari b, Ulhas K Kharul b and Sreekumar Kurungot a*

Figure S1(a-d) shows the representative HRTEM images of HCNF at the P/C ratios of 0.25, 0.5, 1 and 2 respectively. Figure S1a, the HRTEM image of CP-0.25, clearly shows a discontinuous filling of the polymer in the inner cavity along with an uneven coating of the same on the outer surface. In CP-0.5, the coating is rather uniform and the image indicates almost continuous filling in the inner cavity as well (Figure S1 b). However, at higher P/C ratios, as can be evident from Figure S1 c-d, the entire CNF is immersed in the polymer matrix with the individual tubes interconnected by a thick polymer layer. These results indicate that the uniformity as well as the extent of the polymer incorporation varies with the P/C ratios. It is also important to note that at the P/C ratio of 0.5, a uniform coating on the outer surface along with its continuous filling in the inner cavity is formed in CNF. Moreover, at higher P/C ratios, the excess polymer is deposited as agglomerates in the regions away from the CNF surface.
Figure S1. TEM images of (a) CP-0.25, (b) CP-0.5, (c) CP-1 and (d) CP-2 clearly depicting the variation in the extent of the polymer incorporation with different P/C ratios.
Figure S2. Elemental mapping of C, N and O in CP-0.25-700
Figure S3. Elemental mapping of C, N and O in CP-0.5-700
**Figure S4.** Elemental mapping of C, N and O in CP-1-700
Figure S5. Elemental mapping of C, N and O in CP-2-700
Figure S6. EDAX report of a) CP-0.25-700, b) CP-0.5-700, c) CP-1-700 and d) CP-2-700
EDAX analysis and the elemental maps from CP-0.25-700, CP-0.5-700, CP-1-700 and CP-2-700 are given in Figure S2-S5. It is clear from the EDAX analysis that C, N, O and trace amount of Fe are present in all the samples. This slight amount of Fe content detected is from the catalyst used for the CNF synthesis. The nitrogen Wt % obtained from the EDAX analysis in CP-0.25-700, CP-0.5-700, CP-1-700 and CP-2-700 are respectively 5.63, 6.11, 6.77 and 7.57. This increase in the nitrogen percentage in various samples is in accordance with the increase in the precursor amount. However, the EDAX results for the CP-0.25-700 sample taken from two different areas displayed two different nitrogen contents; 5.63 and 4.63. Such an inconsistency in the nitrogen Wt % indicates non-uniform N-incorporation in the sample. The EDAX elemental maps shown in Figure S2-S5 indicate the uniform distribution of C, N and O in all the synthesized products. This demonstrates the homogeneous N-incorporation in CNF.
Figure S7. Rotating disk electrode (RDE) polarization curves obtained for (a) CP-0.5-700, (b) CP-0.5-900, and (c) CP-0.5-1000 in O₂ saturated 0.1M KOH with various rotation rates at a scan rate of 5 mVs⁻¹.
Figure S8. (a) Cyclic voltammogram obtained at a scan rate of 50 mV/s and (b) Rotating disk electrode (RDE) polarization curves obtained at 5 mV/s and at a scan rate of 1600 rpm for CP-0.5-900 in O₂ saturated 0.1M KOH using Pt and carbon counter electrodes.

Figure S9. The Koutecky – Levich plot obtained for (a) CP-0.5-700, (b) CP-0.5-900, and (c) CP-0.5-1000 derived from RDE polarization curves at different electrode potentials.