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Supporting Information

Cumulative effect of transition metals on nitrogen and fluorine co-doped graphite nanofibers: An efficient and durable non-precious metal catalyst for oxygen reduction reaction

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Analysis of total metal content after acid leaching:

Generally, durability of the transition metal catalysts was affected due to metal leach out in acidic environment and is one of the major restrictions which decreased the PEFC performance. The total content of Fe and Co in the catalyst is measured by thermo-gravimetric analysis in air atmosphere carried out in between 35 ^{o}C and 1000 °C with the increment of 5 °C min^{-1} and the data is appended below.

From the data, the residual mass remained for the Fe-Co/NF-GNF catalyst before and after acid leaching were about 8.75 and 7.13 %, respectively. It is interesting to note that after acid leaching, the residual mass is lowered by 1.62 %. The resistance of the metal nanoparticles to the acid leaching could be attributed to the strong M-N-C covalent bonds greatly avoids the detachment of Fe and Co species from the graphene matrix and the metal encapsulation by graphene layers as discussed in the manuscript. As discussed, the high stability and durability of the Fe-Co/NF-GNF catalyst cycled between 0 – 1 V vs RHE and in simulated corrosive test (0.6 V and 1.4 V vs RHE) is due to the high metal content available even after the acid leaching could be the major reason behind high activity of Fe-Co/NF-GNF catalyst.

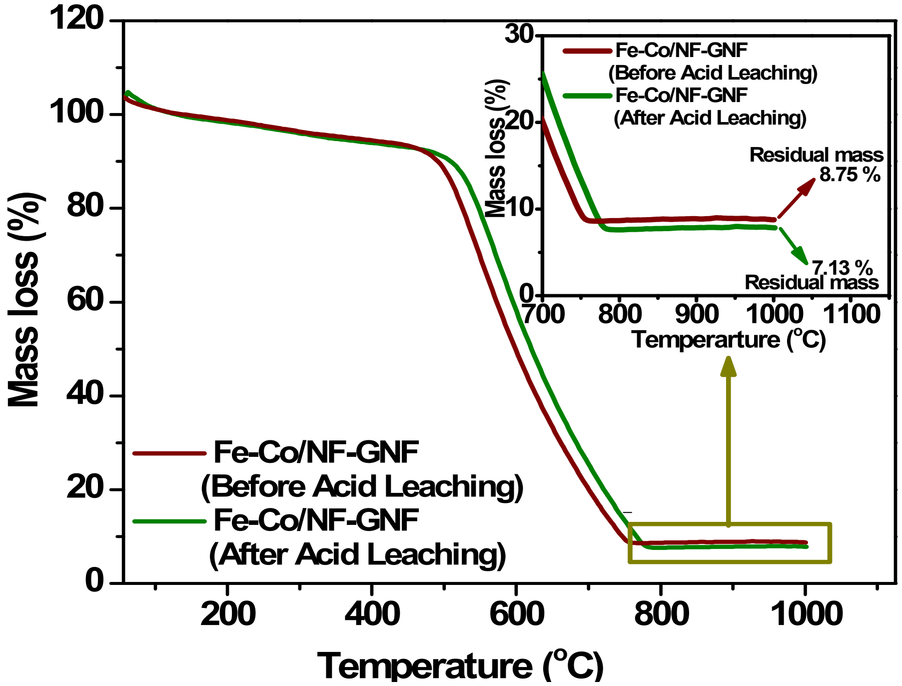

Fig. 1. Thermo-gravimetric analysis of Fe-Co/NF-GNF catalyst before and after acid treatment. Residual mass content of the catalysts are shown in the inset.

Role of F in the Fe,Co/NF-GNF catalyst:

As discussed in our earlier report (**Cited Ref. 37: Carbon 2015, 93, 130-142**), doping of highest electronegative element, such as F induces maximum polarization in the adjacent -C-C- bonds of the hexagonal carbon lattice and in presence of N, the GNF is converting to the graphene structures with many active open edge sites favourable for O_2 reduction. Besides, facilitating ORR, F doping modifies the electron density of the surrounding carbon atoms and increases the thermal and electro-chemical stability of metal nanoparticles. Hence, it can be predicted that the combination of N and F doping would not only increases the ORR activity, it also greatly enhances the durability of the catalyst (**Cited Ref No. 19. ACS catal. 2013, 3, 1726-1729 and Ref No. 49: ACS Appl. Mater. Interfaces 2012, 4, 6728-6734).** As per the reviewer's suggestion, we have also synthesized a catalyst without adding F source (Fe-Co/N-GNF) and evaluated its ORR activity shown below. It is found that, the ORR activity of Fe-Co/N-GNF is 72 mV lower than the Fe-Co/NF-GNF catalyst, calculated at 2 mA cm^{-2} current density. This concludes that the F doping greatly changes the structure of GNF to the graphene and synergistically enhances the ORR activity of Fe-Co/NF-GNF catalyst.

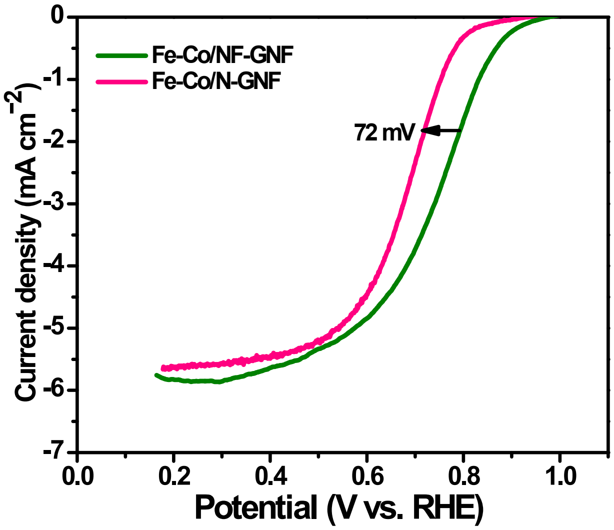

Fig. 2. LSV of Fe-Co/NF-GNF and Fe-Co/N-GNF