We present a detailed study of a novel Fe₃C-based spherical catalyst with respect to synthetic parameters, nanostructure formation, ORR active sites and fuel cell demonstration. The catalyst is synthesized by high temperature autoclave pyrolysis using decomposing precursors. Below 500 °C, melamine-rich microspheres are first developed with uniformly dispersed amorphous Fe species. During the following pyrolysis at temperatures from 600 to 660 °C, a small amount of Fe₃C phase with possible Fe–Nx/C active sites are formed, however, with moderate catalytic activity, likely limited by the low conductivity of the catalyst. At high pyrolytic temperatures of 700–800 °C, simultaneous formation of Fe₃C nanoparticles and encasing graphitic layers occur within the morphological confinement of the microspheres. With negligible surface nitrogen or iron functionality, the thus-obtained catalysts exhibit superior ORR activity and stability. A new ORR active phase of Fe₃C nanoparticles encapsulated by thin graphitic layers is proposed. The activity and durability of the catalysts are demonstrated in both Nafion-based low temperature and acid doped polybenzimidazole-based high temperature proton exchange membrane fuel cells.