

Lignin derived bimetallic platinum group metal-free electrocatalysts for the oxygen reduction reaction in acid and alkaline media

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Hydrogen fuel cells will be crucial to foster the Green Revolution. Proton exchange membrane fuel cells (PEMFCs) have reached unprecedented performance in terms of power output and durability [1]. To further push this technology towards wide commercialization, great effort has been devoted to decrease the amount of platinum used as electrocatalyst on both anodic and cathodic reactions. It is the utilization of platinum and critical raw materials the biggest issue of this technology that is actually slowing down the large scale commercialization. The operations in alkaline media favor the utilization of electrocatalysts that do not contain platinum group metals (PGM-free) [2]. Therefore, in the past 10-15 years a great effort has been invested in developing this class of materials [2]. Since the oxygen reduction reaction (ORR) is sluggish, the majority of the effort has been devoted towards this cathodic reaction.

In this work, we have synthesized mono- and bi-metallic electrocatalysts based on Fe-, Mn- and Fe-Mn-. Particularly, the synthesis comprehends initially the transformation of waste lignin into high surface area conductive carbon (BET of 1300 m²/g). This carbon was then mixed with metallic Phthalocyanine (Fe- or Mn- or both) in percentage in weight of 20% and subject to pyrolysis (600°C for 1 h in N₂/H₂ 95/5 atmosphere). The transition metal phthalocyanine provide both nitrogen and metallic source to provide the desired M-N-C active sites. The obtained electrocatalyst was characterized chemically and morphologically. The electrocatalysts were also tested using rotating ring disk electrode (RRDE) technique in alkaline and acid media.

“Metal-free” lignin derived electrocatalyst was the worst performing in both electrolyte showing low half wave potential and high peroxide produced. MnPc derived electrocatalyst was slightly better performing compared to the “metal-free” electrocatalyst however its performance were still poor with high peroxide produced and low E_{1/2}. The most performing electrocatalyst was the bimetallic Fe-Mn-Pc derived that was slightly better than Fe-Pc derived. In acid media, Fe-Mn-Pc derived electrocatalyst showed a E_{on} of 0.84 V (vs RHE), an E_{1/2} of 0.75 V (vs RHE) and a limiting current of 3.5 mA/cm² with a loading of 0.6 mg cm⁻². The peroxide produced was always below 20%. In alkaline media, Fe-Mn-Pc derived electrocatalyst showed a E_{on} of 0.94 V (vs RHE), an E_{1/2} of 0.88 V (vs RHE) and a limiting current of 4.4 mA/cm² with a loading of 0.6 mg cm⁻². The peroxide produced was low and it increased with the increasing of the overpotentials with a maximum value of 30% at 0V vs RHE.

Durability tests were conducted in alkaline media showed comparable E_{on} and E_{1/2} after 5000 cycles and a decrease in limiting current from 4 mAcm⁻² to 3.2 mAcm⁻². These results indicated that the electrocatalyst is very stable during the operations.

[1] R.K. Ahluwalia, X. Wang, A. Rousseau, R. Kumar. Fuel economy of hydrogen fuel cell vehicles. Journal of Power Sources 130 (2004) 192-201

[2] T. Asset, P. Atanassov. Iron-nitrogen-carbon catalysts for proton exchange membrane fuel cells. Joule 4 (2020) 33-44