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ELECTROCATALYST DERIVED FROM IRON SALT AND BENZ- AND AMINOBENZIMIDAZOLE PRECURSORS: APPLICATIONS IN MICROBIAL FUEL CELL CATHODES.

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Abstract **– In this work, novel catalysts derived from iron and benzimidazole and aminobenzimidazole were synthesized using Sacrificial Support Method (SSM). The catalysts obtained were then tested in rotating ring disk electrode (RRDE) technique and compared with AC. Fe-based catalysts had performances much higher compared to AC and therefore are suitable for microbial fuel cell (MFC) applications. Future works will integrate the catalysts into air-breathing cathodes and test them in MFCs.**

Index Terms **– Oxygen reduction reaction (ORR), platinum group metal-free (PGM-free), neutral media electrolyte, microbial fuel cell (MFC)**

I. INTRODUCTION

Microbial fuel cell (MFC) is an interesting technology capable of degrading organic pollutants and producing useful electricity. In general, the organics are electro-oxidized into carbon dioxide, protons and electrons by electroactive bacteria. Those specific microorganisms colonize the anode electrode and are able to release the electrons from the oxidation reaction directly to the electrically conductive electrode, while protons are simultaneously released into the solution. Electrons move through the external circuit generating useful electricity. The reduction reaction occurs at the cathode in which an oxidant is reduced [1].

For several reasons such as high potential and natural availability at no additional cost, oxygen is the most used oxidant. Due to the high overpotential required for the oxygen reduction reaction (ORR) in neutral media, the addition of the catalyst is needed in order to enhance the sluggish ORR kinetics. Bacterial catalysts suffer from low kinetics and the mechanisms are still debated. Enzymatic catalysts are excellent in neutral media but the low durability discourages the utilization for long terms operations. Abiotic catalysts are then the most preferred catalysts to be adopted in MFC devices. Platinum is a rare and expensive metal, which is easily can be poisoned in polluted environment and consequently is not suitable for MFCs applications. Despite the fact that high surface area carbonaceous materials can be an alternative to substitute Pt, their performances are low. Recently we reported that platinum group metal-free (PGM-free) catalysts seem to be very promising alternatives to Pt due to their high activity in neutral media and high stability to the poisonous environment [2,3]. Those catalysts are based on the utilization of atomically dispersed transition metals coordinated with nitrogen inside of 3D carbon matrix.

In this work, two novel iron based catalysts pyrolyzed using benzimidazole and aminobenzimidazole as nitrogen rich organic precursors were synthesized and studied in rotating ring disk (RRDE) electrode in neutral media. Further studies will be developed for incorporating those catalysts in air-breathing cathodes and tested in operating MFCs.

II. MATERIAL AND METHOD

Two novel PGM-free Fe-N-C catalysts using sacrificial support method (SSM). Iron nitrate was mixed with benzimidazole and aminobenzimidazole respectively and then also with monodispersed silica used as template. The mixture was pyrolyzed at controlled temperature furnace at 900°C. The powder was inserted into a quartz tube in which inert atmosphere was present (UHP nitrogen) with a flow of 100 cm^3min^{-1}. After 45 minutes at stable temperature, the quartz

tube was left to cool down till room temperature was reached. After this procedure, the powder was treated with HF in order to remove the silica template and create a catalyst three-dimensional structure. The powder was then washed to remove the HF and then dried. The last step consisted in grinding the catalyst using ball-milling.

Rotating ring disk electrode (RRDE) was used to study the catalyst kinetics towards ORR in neutral media. Two loadings of catalysts were applied (0.1 and 0.6 mg cm^{-2}). Activated carbon (AC) was used as control. The inks were applied on the disk and naturally dried. The electrolyte used was potassium phosphate buffer with pH of 7.5. The electrolyte was purged with oxygen before the utilization. The disk speed was 1600 rpm. Linear Sweep voltammetry (LSV) was run between 1 V and 0 V (vs RHE).

III. RESULTS

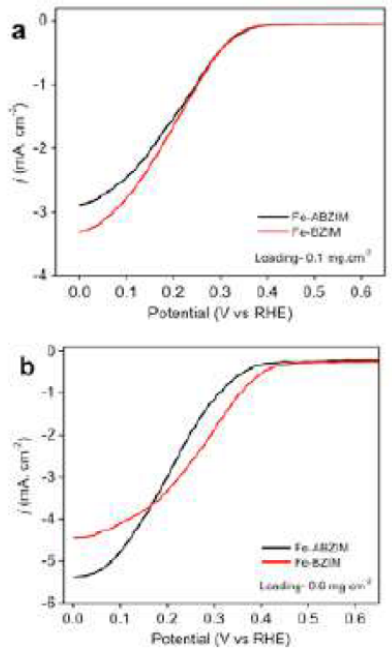

Fig.1 Disk current of two different loadings: 0.1 mg cm^{-2} (a) and 0.6 mg cm^{-2} (b).

LSVs shows that both Fe-ABZIM and Fe-BZIM performed better than AC since their onset potential, half wave potential and limiting current were superior compared to AC. The loading did not affect the trends despite an increase in loading brings to an increase in the half wave potential (**Fig. 1**). From those results, it can be noticed that Fe-BZIM had slightly higher electrocatalytic activity compared to Fe-ABZIM. Fe-BZIM had an half wave potential of ~0.22 V (vs RHE) and ~0.28 V (vs RHE) at catalyst loading of 0.1 and 0.6 mg cm^{-2} respectively. In parallel, Fe-ABZIM had half wave potential of ~0.23 V (vs RHE) and ~0.22 V (vs RHE) at catalyst loading of 0.1 and 0.6 mg cm^{-2} respectively.

Peroxide production and electron transfer were also monitored (data not shown). The highest peroxide production was detected for AC while the lowest was measured for Fe-BZIM (≈4%, loading 0.6 mg cm^{-2}). It can be noticed that the peroxide produced generally decreased with the increase in catalyst loading. This might be due to the peroxide trap and further reduced within the thick catalyst layer. In parallel also the electron transfer tends to have a 4e- mechanism with the number of electrons that increases with the loading indicating a more probable 2x2e- mechanism.

Further investigations will focus on the integration of those catalysts in air-breathing cathodes and operated in microbial fuel cells. The performances will be compared with the performances of activated carbon catalyst that is by far the most utilized cathode in literature.

IV. CONCLUSION

Oxygen reduction reaction kinetics study of Fe-based catalyst was performed in neutral media. Fe-BZIM and Fe-ABZIM performed much better compared to AC in terms of onset potential, half wave potential and limiting current. Those catalysts will be tested in microbial fuel cells once integrated in air-breathing cathodes.

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