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Cost Effective Non Precious Metal Catalyst for Application in Fuel Cells

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Abstract— **Hydrogen is a versatile fuel that can power almost anything. Fuel cells are an energy conversion device that can harness the power of hydrogen. A fuel cell produces electricity through a chemical reaction, but without combustion. It converts hydrogen and oxygen into water, and in the process also creates electricity. It's an electro-chemical energy conversion device that produces electricity, water, and heat. A proton exchange membrane fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, as opposed to the direct combustion of hydrogen and oxygen gases to produce thermal energy. A stream of hydrogen is delivered to the anode side of the MEA (Membrane Electrode Assemblies). At the anode side it is catalytically split into protons and electrons. In this article, the various types of non precious metal catalysts that can be used as an alternative to expensive precious metal catalysts have been discussed. Over the years several classes of non precious metal catalysts have been identified and developed that reduces the cost of production. Non precious metal catalysts enhance the catalytic activity for oxygen reduction reaction and reduce the cost of the reaction. Light has been given upon the catalytic activity of such non precious metal catalysts.**

Index Terms— **PEMFC, non precious metal catalysts, cost, oxygen reduction reaction**

I. INTRODUCTION

Fuel cells generate electricity by an electrochemical reaction in which the energy is released electrocatalytically. This allows fuel cells to be highly energy efficient, especially if the heat produced by the reaction is also harnessed for space heating, hot water or to drive refrigeration cycles. A fuel cell uses an external supply of chemical energy and can run indefinitely, as long as it is supplied with a source of hydrogen and a source of oxygen (usually air). The reactions that produce electricity take place at the electrodes. Every fuel cell also has either a solid or a liquid electrolyte, which carries ions from one electrode to the other, and a catalyst, which accelerates the reactions at the electrodes.

The proton exchange membrane fuel cell (PEMFC) uses a water-based, acidic polymer membrane as its electrolyte. PEMFC cells operate at relatively low temperatures and can tailor electrical output to meet dynamic power requirements. Due to the relatively low temperatures and the use of precious metal-based electrodes, these cells must operate on pure hydrogen. Hydrogen fuel is processed at the anode where electrons are separated from protons on the surface of a catalyst. The protons pass through the membrane to the cathode side of the cell while the electrons travel in an external circuit, generating the electrical output of the cell. On the cathode side, another metal electrode combines the protons and electrons with oxygen to produce water, which is expelled as the only waste product; oxygen can be provided in a purified form, or extracted at the electrode directly from the air.

Non precious metal catalysts have been of great importance now. Such catalysts accelerate the reaction and also reduce the production cost. A new class of low-cost (non-precious metal) nanocomposite catalysts for the PEMFC cathode, capable of combining high oxygen-reduction activity with good performance durability are being used. The non-precious metal in the acidic environment of the PEMFC cathode not only stabilize the reaction but also generate active sites for oxygen reduction reaction. The high price of precious metal catalyst creates a major cost barrier for large-scale implementation of polymer electrolyte membrane fuel cells. Non precious metal catalysts (NPMCs) represent attractive low-cost alternatives. Since precious metal is expensive and there are limited worldwide reserves, technologies that could substantially reduce or replace its use have to be realized before widespread PEMFC commercialization. Highly active catalyst is needed to promote both the fuel oxidation at the anode and oxygen reduction at the cathode. Much research is being carried out to identify and develop non precious metal catalyst as alternatives.

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II. TYPES OF NON PRECIOUS METAL CATALYST

Transition metals-

Transition metal elements in the periodic table are referred to as non-precious metals (NPMs). This includes nickel, iron, cobalt, chromium, copper, tungsten, selenium and tin which have all been found to have some activity for catalysis of the reaction. Transition metals supported on porous carbons, have demonstrated reasonable electrocatalytic activity. These non-precious metals are used as catalysts in the form of transitional metal complexes such as chalcogenides, transition metal oxides or nitrides and macrocycles.

Iron-based nanostructures-

Iron-based nanostructures on nitrogen-functionalised mesoporous carbons are beginning to emerge as possible contenders for future commercial PEMFC systems.

Alloys-

Precious metals such as Pt, Pd, Ru alloyed with non precious metals have been investigated for use as catalysts.

Macrocyclic compounds-

One of the major catalysts that have been researched is transition metal macrocyclic compound. The complexes with cobalt and copper have been investigated to be most stable. The best combination of stability and activity is seen with cobalt and iron.

Carbon support-
Carbon-supported Fe Co catalyst, produced by pyrolysis of CoTMPP in the presence of iron oxalate has been reported and patented by Hilgendorff et al. They claim that the catalytic activity is almost identical to that of a conventional standard catalyst material employing platinum.

Electroconductive polymer-
Electroconductive polymers are synthesized with conjugated heterocyclic polymers such as polyaniline, polypyrrole and poly (3-methylthiophene (P3MT)). Such polymer tends to act as catalyst in the oxygen reduction reaction.

Nitrides-
Non precious metals modified with nitrides are seen as potential catalysts. Molybdenum nitride and tungsten nitride have been investigated for use as catalyst. It has been shown that the catalyst has significant electrocatalytic activity for the oxygen reduction reaction.

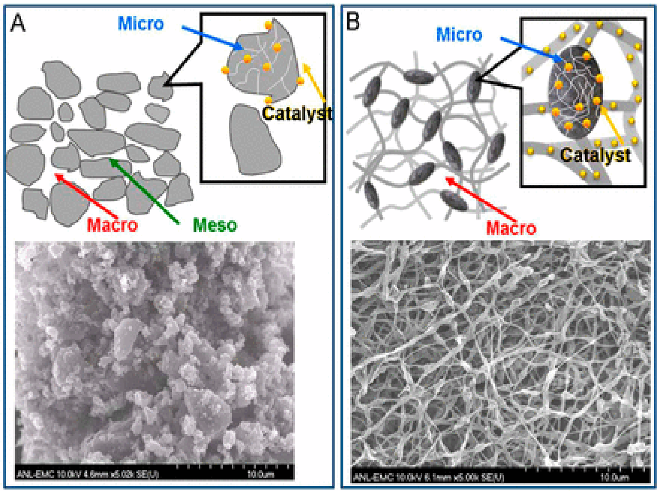
Carbon catalysts-
Functionalised carbons, or metals supported either directly on carbon or carbon activated with nitrogen have been researched for use as catalyst. Carbon support functionalised with nitrogen is used to synthesise the macrocyclic-like structures that features metal-nitrogen bonding that are known to catalyse the reaction.

III. CATALYTIC ACTIVITY

A major limitation of PEMFC is the expense associated with precious metals used as catalysts. Pyrolised transition metal nitrogen carbon catalyst can be used as an alternative, but they tend to show lower activity and stability as compared to precious metals. Thus pyrolysis of catalyst should be done on such a way that it maximize the number of sites on the catalyst surface and hence maximize the catalytic activity towards oxygen reduction reaction. It has been seen that the catalytic activity towards oxygen reduction reaction can be improved by increasing the concentration of nitrogen.

Transition metal and N-doped carbonaceous composites have shown promising oxygen reduction reaction catalytic activities in both acidic and alkaline media, while transition metal-free composites have shown activities primarily in an alkaline medium. New surface property and synthesis strategies are being identified for continuously improving catalytic activity. Lefèvre identified that the catalytic activity of oxygen reduction reaction can be enhanced by infiltrating the N-coordinated iron complex within the micropores (pore diameter <2 nm) of the carbon support.

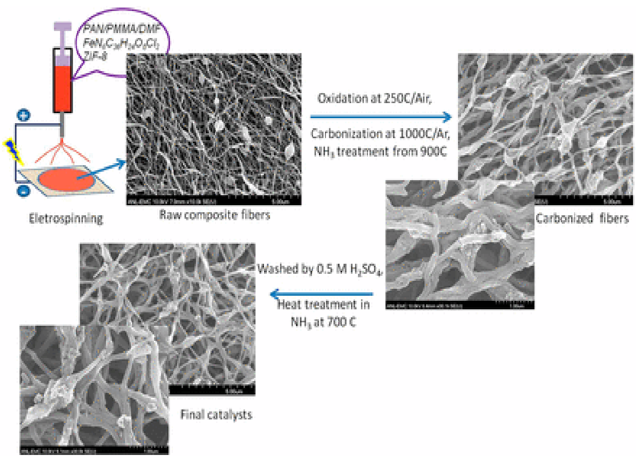
Various new synthetic approaches are investigated to produce high catalytic active site density decorated within the micropores using rationally designed zeolitic imidazolate frameworks (ZIFs) and porous organic polymers. Although the micropore is critically important in hosting active site for oxygen reduction reaction, the catalyst should also contain a sufficient amount of macropores (pore size >50 nm) to ensure the effective mass transfer of both reactant (O_2) and product (H_2O) to and from the active sites with minimal resistance throughout the entire electrode layer. The micropores reside inside of primary carbon particles in a conventional amorphous carbon support with the dimensions of a few tenths of a nanometer. The large cluster mesopores are formed in the space between them by the agglomeration of the carbon particles by van der Waals force. The macropores are generated by the voids through further stacking of these clusters. The mesopores, serve as the secondary passage between the gas phase to catalytic site in micropores, and create additional tortuosity, and hence mass-transfer resistance within each cluster. Mesopores also have much higher volume-to-surface area ratios than the micropores. Therefore, they add substantial volume to the catalyst and reduce the electrode volumetric current density.

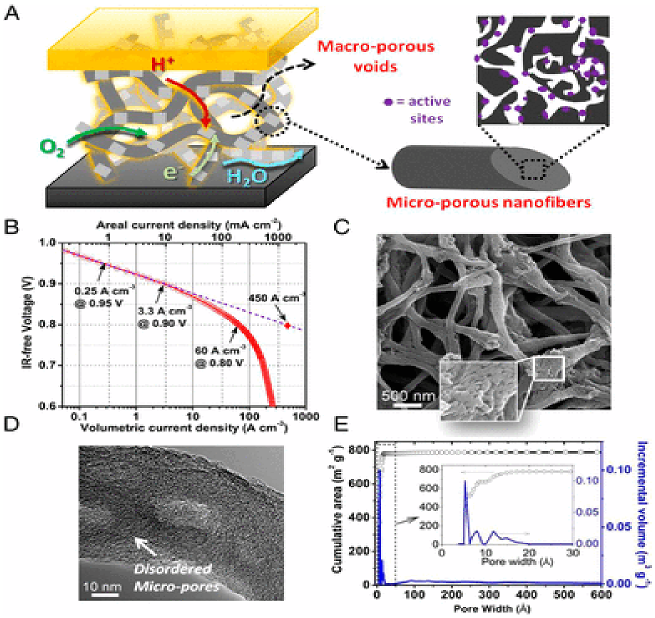


[A] conventional carbon support [B] nanonetwork catalyst

IV. SYNTHESIS METHOD OF NON PRECIOUS METAL CATALYST

Interconnected porous nanonetwork catalyst-
An interconnected porous nanonetwork catalyst can be produced by electrospinning a polymer solution containing Tris-1,10-phenanthroline iron(II) perchlorate (TPI) and ZIFs, a subgroup of metal–organic frameworks (MOFs), followed by posttreatments.





[A] A schematic drawing of macropore–micropore morphology and charge/mass transfers in the nanofibrous network catalyst at the fuel cell cathode.
[B] Plot for the kinetic activity of Fe/N/CF obtained from a single fuel cell test.
[C] SEM image of the Fe/N/CF nanonetwork catalyst.
[D] High-resolution TEM image of a thin catalyst fiber.
[E] BET isotherm analyses on cumulative surface area and incremental pore volume as the functions of pore size in Fe/N/CF.

MEA preparation and PEMFC tests-
For the preparation of catalyst ink the catalyst after the pyrolysis, acid wash, and ammonia treatment was mixed with Nafion ionomer diluted by isopropanol/water solvent. A smooth ink is evenly coated over each fiber . The prepared cathode and anode are hot-pressed onto the opposite sides of a Nafion to make the final MEA.

Rotating-ring disk electrode-
RRDE is a rotating ring disk electrode that can be used to perform electrochemical measurements under controlled hydrodynamic conditions. The ring and disc electrode assembly provides the means to detect reaction intermediates *in situ* through collection experiments. The RRDE is an important tool for characterizing the fundamental properties of electrocatalysts used in fuel cells.

Physical and Chemical Characterizations-
Catalyst composition can be investigated by inductively coupled plasma optical emission spectroscopy. The catalyst surface area and pore size distribution were measured by the BET method and pore size analyzer. Catalyst morphologies can be characterized by SEM and TEM.

A. *USEFUL ALTERNATIVE*

Although precious metal catalysts are the most important material in fuel cell applications, the costs of these catalysts contribute by 33 % to the overall costs of a fuel cell stack. Thus it is reasonable to search for cheap alternatives, such as non-precious metal catalysts (NPMC). Some metal nitrides (Me = W, Mo) and oxynitrides (Me = Ta, Zr, Nb) are promising regarding the observed onset potentials and are a matter of interest for further investigation. Metal-nitrogen-carbon catalysts are at present the best performing non precious metal catalysts for oxygen reduction reaction.

A major problem with commercialization of PEMFC is the high content of supported platinum electrocatalysts used for oxygen reduction and the cost involved. Since platinum is an expensive metal of low abundance, it has been of intense interest for researchers to develop a corrosion resistant non precious metal substitutes. In the last few years, several transition metal compounds have been proposed as oxygen reduction reaction (ORR) selective catalyst.

The RRDE (Rotating-ring disk electrode) is an important tool for characterizing the fundamental properties of electrocatalysts used in fuel cells. When oxygen in PEMFC is reduced using an electrocatalyst, an unwanted and harmful by-product, hydrogen peroxide may be produced. Hydrogen peroxide can damage the internal components of a PEMFC. An RRDE "collection experiment" can be used to probe the peroxide generating tendencies of an electrocatalyst. Here the disk is coated with a thin layer bearing the electrocatalyst, and the disk electrode is poised at a potential which reduces the oxygen. Any products generated at the disk electrode are then swept past the ring electrode. The potential of the ring electrode is poised to detect any hydrogen peroxide that may have been generated at the disk. Rotating-ring disk electrode (RRDE) voltammetry can be used to examine the catalytic activity of the complexes on a carbon support in acidic media, imitating fuel cell performance.

V. BENEFITS OF FUEL CELL

Health Benefits-
Since hydrogen fuel cells produces only heat and water and no toxins, particles, or greenhouse gasses, clearer air is available for us to breathe.
Environmental impact-
Since hydrogen fuel cells do not produce air pollutants or greenhouse gasses, they can significantly improve our environment.
Complementary-
Fuel cells can readily be combined with other energy technologies, such as batteries, wind turbines, solar panels, and super-capacitors.
Versatile-
Fuel cells are scalable, and provide everything from milliwatts to megawatts of power in a variety of uses - from cellphones, to cars, to entire neighbourhoods.

VI. CONCLUSION

Since fuel cells produce electricity from the energy of a fuel through electrochemical process, it results in low emissions and less environmental impact. The use of the precious metal platinum as the catalyst for the anode and cathode is one of the impediments to widespread PEMFC commercialisation on account of its high cost and scarcity. Thus researchers around the world are encouraged to look for alternative materials that are cheaper and yet perform better or equivalent to the Pt standard. The production of lower cost oxygen reduction reaction catalysts by developing a better understanding of electrocatalysis for the oxygen reduction reaction is vital for continuous improvement and further development of PEMFC technology. Of the precious metals, platinum has the highest electrocatalytic activity for oxygen reduction at the cathode of PEMFC.

Several types of non precious metals can be used as catalysts towards oxygen reduction reaction in PEMFC (Proton Exchange Membrane Fuel Cell). Hence the central idea is to identify and develop non precious metal catalyst that not only accelerate the oxygen reduction reaction but also brings down the cost.

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