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Synthesis of Ni Nanotubes for Enhanced Oxygen Reduction Reaction at Cathode Side of PEM Fuel Cell

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***Abstract*—** Electrocatalytic activity at cathode side in Polymer Exchange membrane fuel cell (PEMFC) is sluggish and requires an active catalyst. Untill now Platinium (Pt) is considered as the most feasible and active catalyst for Oxygen reduction reaction at cathode. It is most expensive and also faces the problem of poisioning due to carbon monoxide, hence a more reactive, durable catalyst is required to meet the demand for commercialization. In this study a novel non platinum group metal (N-PGM) Ni nanotubes were prepared by using Solvothermal technique using transition metal precursor with profound insight.Ni nano tubes were obtained after pyrolyzing Ni Zeolitic Imidazolate Framework (Ni/ZIF) at 800 0C under inert nitrogen atmosphere.It's electro catalytic performance was examined by Linear Sweep Voltammetry (LSV), done with Rotating Disk Electrode (RDE) evaluation showing that Ni nanotubes owns splendid electro catalytic behavior for Oxygen Reduction Reaction (ORR) in basic environment. It depicts a current density of -2.6mA/cm2 and an over potential of -0.28V Vs. Saturated Calomel Electrode (SCE), and RDE Results were obtained at 400,800,1200 and 1600 rpm in 0.1M KOH solution while the Ni/ZIF shows the minimum current density of -1.4 mA/cm2..The Pt/C catalyst was also analyzed in the same environment for comparison purpose having a current density of -4.6 mA / cm2. The results reflect that Ni nanotubes is promising catalyst for Proton exchange membrane (PEM) fuel cell.

***Keywords*—** Proton Exchange Membrane (PEM) Fuel cell, Zeolitic Imidazolate Frameworks (ZIF-67), Ni nanotubes.

I. INTRODUCTION

Proton Exchange Membrane Fuel Cell (PEMFC) is a promising technology for conversion of fuel (Hydrogen) to electricity with much higher efficiency than internal combustion Engine. PEMFC is an outstanding device to hamper the Global pollution, it is a credible technology for economical Energy. However, high cost is the main hurdle in its commercialization [1] and the cost mainly comes from the catalyst part of the fuel cell, which uses precious metals (Pt, Ru), another problem is the sluggish oxygen reduction reaction (ORR) at cathode side in PEMFC's. A number of materials were researched to enhance the ORR activity, among them Platinum (Pt) has shown the highest ORR activity and stability till date. Silver (Ag) was meticulously studied due to its abundance, low cost and high activity, but half wave potential of Ag in Rotating disk electrode (RDE) is lower than Pt [3].Pt, Ru showed higher ORR activity but it is precious and more prone towards CO poisoning. Alloying of transition metals (Co,Fe,Cu,Ni) impart synergistic effect to Pt. The d band center of Pt goes down with alloying, hence dwindling the bonding energy of Pt with oxygenated species [2]. K.Yang et al discovered a new material Nano particles PtFe Nitrogen doped carbon sheets (np-PtFe/NPCS) having three time higher current density and more positive half wave potential than Pt/C[4]Y. Haoran et al uses a non Pt catalyst for ORR and found its activity better than the commercial Pt/C catalyst. For alleviating our dependence on the precious metals (Pt, Ru) for ORR, more attention were given to develop Non platinum group metals (NPGM) catalysts. H.Jang et al produced Metal organic frame work (MOF) having thermally robust and nonporous structure, enhancing surface area for reaction [5].Zeolitic imidazolate frameworks (ZIF's) is a subclass of MOF has enormous potential for preparation of nanotube catalyst, rich in carbon and nitrogen [6,7].Transition metal carbon nanotubes (Pt-Co CNTs, CoCNT) were developed from ZIF precursors to impart porosity and enhance the catalytic effect of transition metals[8,9,10]. H.Zhang et al investigated Ni catalyst activity alloyed with Co and CNTs (NiCo2O4/CNTs hybrid) which showed higher performance than alone Ni,Co and CNT.

In this study a new material, Ni nanotubes were synthesized and tested in alkaline solution. Linear sweep voltammetry (LSV) with RDE evaluation were performed to study and analyzed the ORR electro catalytic activities of Ni-nanotubes. To the best of our cognition this report may be the 1st one on the ORR catalysis by Ni-nanotubes prepared by hydrothermal treatment.

II. MATERIALS AND SYNTHESIS

A. Preperation of Ni/ZIF

Ni/ZIF samples were prepared as given in the literature [12].In the synthesis method, 5.5 g of 2-methylimidazole (2-MIM) was dissolved in 20 ml DI water in one beaker and in another beaker 0.238 g of Nickel (ii) nitrate hexahydrate was also dissolved in 3ml of DI water, a greenish solution is formed. These two solutions were mixed together and constantly agitated for 6 h at room temperature and atmospheric pressure to complete the reaction as much as possible. Then the mixture is transferred to autoclave and maintained at 140 0C under pressure for 24 hour. The sample after removing from autoclave were transferred to centrifuge and orange precipitate were accumulated and washed with water and ethanol alternatively for many time and dehydrated at 80 0C for 24h. The Ni/ZIF was also prepared by this method but it was not sintered and simple Ni/ZIF sample were collected for comparison purpose.

B. *Sythesis of Ni Catalyst*

Ni nanotubes specimen were prepared by the method shown in the literature. The dried ZIF-67 samples were heated up at 350 0C for 1.5 h then the temperature is increased to 800 0C at a ramp rate of 5 0C per minute for 3.5 h at Nitrogen atmosphere reflux (Fig 1) after preparing the black powder, it is cooled down to ambient temperature automatically, then it was treated with 0.5 M H2SO4 solution for 10 h. the catalyst which is prepared were accumulated by high centrifugation, recurrently cleaned with DI water and dehydrated at 100 0C under vacuum atmosphere for 2-3 hour. The Ni nanotubes were collected for experimentation. The method of preparation is described in Fig 1.

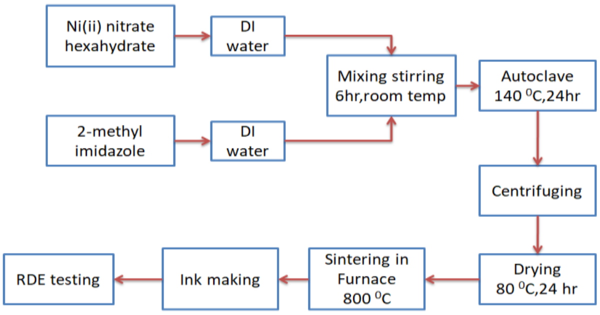

Figure 1. Synthesis steps of Ni nanotubes

C. *Electrode Preparation*

The Catalytic sample was synthesize by scattering 7.5mg of Ni nanotubes sintered specimen in 7.6 ml of deionized (DI) water,2.4 ml Isopropanol alcohol and 40µl of Nafion were dispersed to the ink and sonicated for 20 min in cold water bath of sonicator [13]. In other two vile Ni/ZIF and Pt/C sample were synthesized by same process of scattering the sample in DI water. The thin catalytic layer was generated by dropping a required amount of ink onto the polished glassy carbon disk (4mm in dia, AFE32040GC, Pine Instruments).

For comparison purpose all the catalytic layer were prepared one by one and tested in the same environment in RDE, a homogeneous and stable catalyst layer were prepared by rotation and dehydrated air at room temperature for 20 minute for all the three catalyst [13]. RDE evaluation were done in 0.1 M KOH with oxygen saturated [15]. LSV evaluation were performed Vs SCE at 20 mVs-1 rate having Pt coil as the opposite electrode and SCE as the reference electrode using a PAR Bistat at different revolution, at room temperature. In order to find the strength and durability of the generated Ni nanotubes catalyst film, LSV were performed for 1000 time revolution to evaluate the degradation of the layer and to analyze the change in the current density.

D. *Characterization*

The Fig 2 shows the magnified image of the Ni nanotubes. The image indicates that the nanotubes are formed after the sintering of the Ni/ZIF at high temperature in Nitrogen atmosphere, the width of the nanotubes is of various sizes ranges from 40-70 nm and having larger length than its width. The enhanced reactivity is due to the nanoparticles formation, having increased surface area.

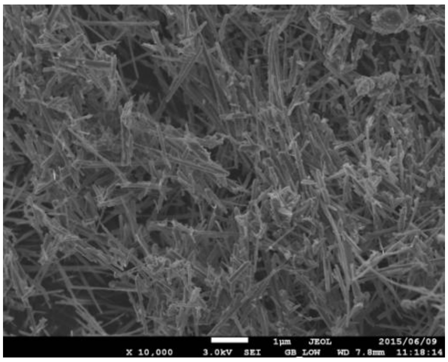

Figure 2. Scanning electron micrograph of Ni nanotubes

III. RESULTS AND DISCUSSION

In order to evaluate the performance of Ni nanotubes towards ORR performance, kinetic mechanism and durability, the electrode were manufacture and LSV experiment were performed in a three electrode system in 0.1 M KOH electrolyte. For comparison purpose the RDEs with Ni/ZIF and Pt/C commercial catalyst were also conducted at similar environment. Figures 3, 4, 5. shows the ORR activity of Ni nanotubes, non sintered Ni/ZIF and commercial Pt/C catalysts in O2 saturated electrolyte at different rpm respectively.

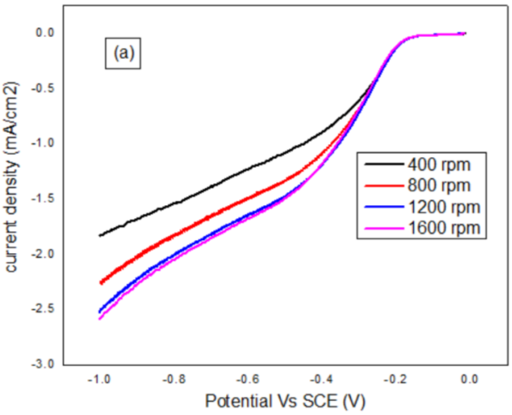

Figure 3. RDE data of Ni nanotubes

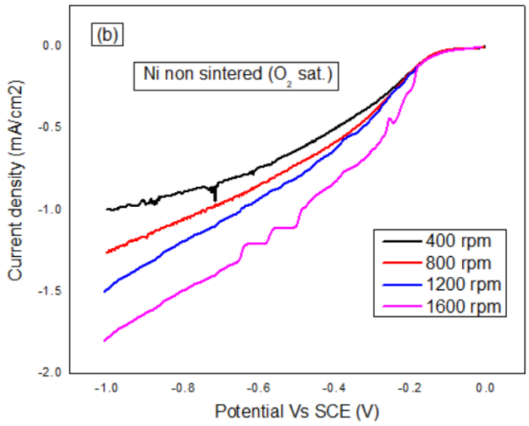

Figure 4. RDE data of Ni/ZIF non sintered

Fig.3 shows the ORR activity of Ni nanotubes at 400, 800, 1200, 1600 rpm in oxygen saturated electrolyte. The current density reaches -2.6 mA/cm2 at 1600 revolution (rpm).the current density slowly increases from 400 rpm to maximum at 1600 rpm.

While the current density of non sintered Ni/ZIF at same environment reaches to -1.7 mA/cm2 at 1600 rpm (Fig 4), which reflects that the activity enhances with the heat treatment of the Ni catalyst. This is due to the expected formation of nanotubes, increasing the surface area for catalytic activities.

The Pt/C catalyst has the highest current density of -4.6mA/cm2 shown in Figure 5. at same environment which is high enough but due to the abundance of Ni and is non-precious it's loading can be increases to acquire the required activity. Fig 6. shows the comparison of all these three catalysts, in which it is indicated that the Pt/C catalyst has the highest current density of all but Ni nanotubes have also greater current density than non sintered Ni/ZIF,clearly indicating the treatment effect on the Ni catalyst. The activity increases, when Ni is sintered.

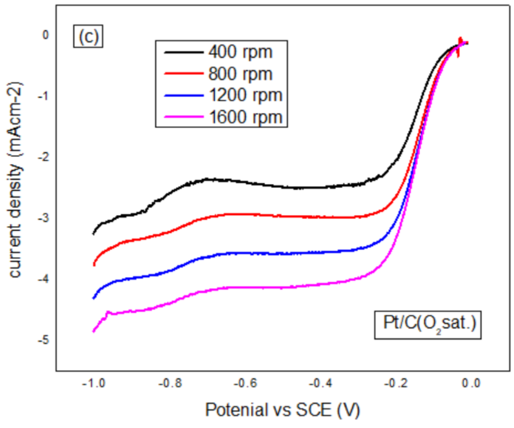

Figure 5. RDE data of Pt/C all at various rpm

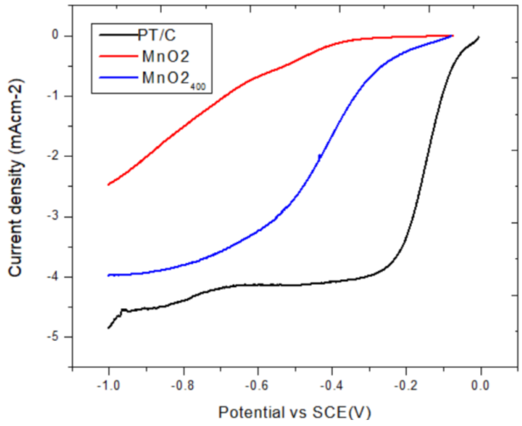

Figure 6. Comparison of Ni nanotubes, Ni ZIF and Pt/C at 1600 rpm

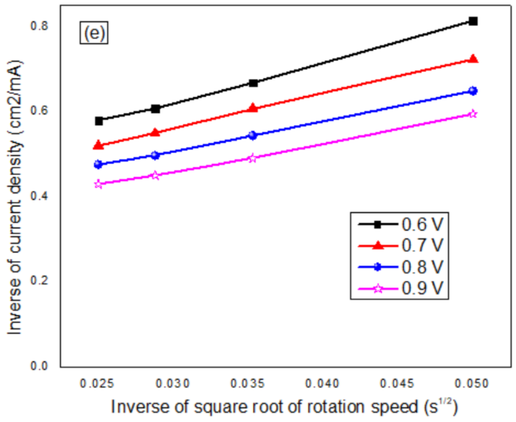

Figure 7. K-L plot for Ni nanotubes at various potentials

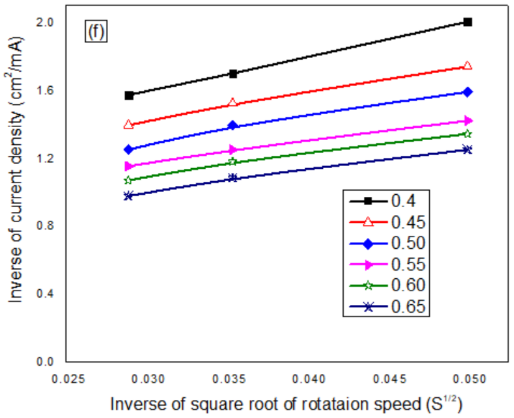

Figure 8. K-L plot for Ni ZIF at various potential

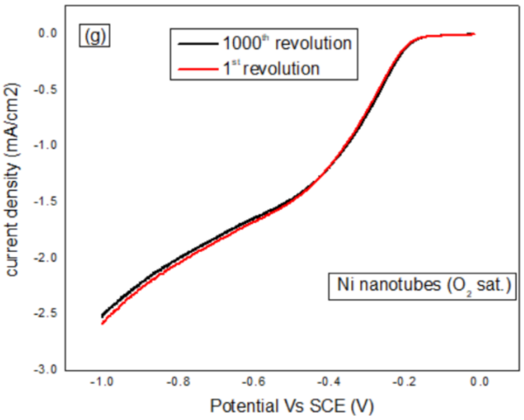

Figure 9. LSV data for Ni nanotubes showing degradation after 1000th cycle

Fig 7. Shows the K-L plot acquired from RDE data on ORR for Ni nanotubes at a number of revolution in oxygen concentrated electrolyte. The extrapolation of the K-L line gives us an intercepts adjacent to zero (0), which demonstrate that the process of oxygen (O2) reduction is totally under the diffusion control, and the slop B can be easily measured.

The electron transfer number is then calculated by the equation 1 to 4.While Fig 8. shows the K-L plot for the Ni ZIF,it clearly shows that the intercept is above zero and also the charge transfer number comes between 2 and 4,which indicate that there is also indirect conversion through hydrogen peroxide.Fig 7. shows that the value for oxygen reduction potential (ORR) for Ni nanotubes approaches to 4 at higher potential, showing direct ORR to water without any peroxide generation in this potential range [14].

To know about the kinetics of electron transfer of Ni nanotubes and Ni ZIF during the ORR, we studied the reaction kinetics by rotating disk voltammetry. The voltammetry profile in O2 saturated 0.1 M KOH electrolyte shows that the current density is enhanced by an increase in rotation rate from 400 to 1600 (Fig 3.)

The corresponding Koutecky-Levich plots (J-1 Vs ϖ-1/2) at different electrode potentials (Fig 7) depicts good linearity and parallelism of the plots are considered as example of first order reaction kinetics in regard to the concentration of mixed O2. The kinetic parameters can be examined on the basis of Koutecky-Levich equations:

$$1/J = 1/J_L + 1/J_K \quad (1)$$

$$= 1/B\ \varpi^{-1/2} + 1/J_K \quad (2)$$

$$B = 0.62\ N\ F\ C_0\,(D0)^{2/3}\,\upsilon^{-1/6} \quad (3)$$

$$J_K = n\ F\ k\ C_0 \quad (4)$$

In which J is the measured overall current density, J_K and J_L are the kinetic and diffusion- Limiting current densities, ϖ is the angular velocity of the disk (ϖ =2πN, N is the linear rotation speed), n is the overall charge transferred number in oxygen reduction, F is the Faraday constant (F = 96485 C mol^{-1}), C_0 is the bulk concentration of O_2 , υ is the kinematic viscosity of electrolyte, and k is the electron transfer rate constant, As from the Fig 7. the charge transfer number(n) and J_K can be calculated from the slop and intercept of the Koutecky-Levich plots. Respectively, and by using parameters $C_0 = 1.2 \times 10^{-3}$ mol L^{-1}, $D_0 = 1.9 \times 10^{-5}$ cm $s^{-1}$and $\upsilon = 0.1$ m^2 s^{-1} in 0.1 M KOH. ORR will either occur via the 4 electron reduction pathway where O_2 is reduced to water or the 2-electron reduction pathway where it is reduced to hydrogenperoxide (H_2O_2).In fuel cell the 4-electron direct pathway is desirable [11].

CONCLUSIONS

Ni nanotubes were prepared by hydrothermal treatment and by sintering at 800 0C in Nitrogen neutral environment. As vividly illustrated from RDE analysis, the Ni nanotubes catalyst illustrates extra ordinary catalytic behavior towards ORR compared to the Ni ZIF and also showed good activity if compared to other catalyst although it is lower than Pt/C catalyst but this can be resolved by heavy loading. It is shown from LSV that the degradation is very low even after several hundred cycles and the catalyst is stable in comparison to Ni ZIF under identical condition. The catalyst shows higher ORR and seemed to be good catalyst for oxygen reduction at cathode side.

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