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Research paper

Oxygen Reduction Reaction of Carbon Nanotubes Supported Polypyrrole Doped Toluene Sulfonic Acid in Alkaline Medium

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Abstract

In this study, polypyrrole/toluene sulfonic acid-based nitrogen doped carbon nanotube (NCNT) is synthesized via chemical oxidative polymerization followed by high-temperature heat treatment under N_2 atmosphere. The structure, morphology and composition of the NCNT catalyst are investigated with X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. Different N species including pyridinic, pyrrolic, graphitic, and oxidized-N are quantitatively determined by X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity of NCNT towards oxygen reduction reaction (ORR) in alkaline condition is evaluated with cyclic voltammetry (CV) and rotating disk electrode (RDE). The globular and tubular structure of NCNT can be clearly seen from SEM images. The typical Raman spectrum for NCNT showed two prominent bands around 1348 cm^{-1} (D band) and 1568 cm^{-1} (G band). High-resolution XPS spectrum of N 1s for NCNT showed that graphitic-N has the highest percentage (39.36%), whereas the pyridinic-N (26.54%), pyrrolic-N (18.88%) and oxidized-N (15.22%). The ORR electrocatalytic activity of the NCNT in 0.1 M KOH has the onset potential of -0.154 V vs. Ag/AgCl, the current density 0.455 mA/cm^2, and electron transfer number of $n \approx 4$.

Keywords: *alkaline medium; oxygen reduction reaction; carbon nanotube; polypyrrole; toluene sulfonic acid*

1. Introduction

Development of new and sustainable energy sources is one of the major topics in recent years due to rapidly growing energy demand and environmental pollution. Currently, fuel cells are considered as one of the cleanest and the most efficient technologies for generating electricity because they can convert chemical energy from fuel into electricity [1]. However, the performance of fuel cells is hampered by the sluggish kinetics of the cathode oxygen reduction reaction (ORR), which cause the low cell potentials [2-3]. Although Pt has been considered as an effective electrocatalyst for ORR, the cost of Pt is a major barrier and it suffers from CO poisoning. Therefore, the development of inexpensive catalysts to replace Pt for fuel cells has attracted great interest in recent years.

To replace the precious Pt catalyst, numerous efforts have been made in recent decades [4-8]. Among various candidates, nitrogen-doped carbon nanomaterials, such as carbon nanotube [9], graphenes [10], graphites [11], graphitic [12], and amorphous carbon [13] showed potential as non-metal electrocatalysts for ORR in fuel cells application. Among these carbon nanomaterials, carbon nanotubes (CNT) have been widely used as a non-metal catalyst in fuel cell applications due to high electrical conductivity, good chemical and thermal stability [14]. This high electrical conductivity of CNT can facilitate electron delivery to the active site, making oxygen reduction fast and efficient. In addition, nitrogen-doped CNT has showed a high electrocatalytic activity towards ORR in alkaline medium [6]. Other than that, many researchers found that the bonding configuration of N-atoms incorporated to the surface of carbon materials is important for the electrocatalytic activity towards ORR [15-16]. They also pointed out that the amount of nitrogen in the catalyst material and the nature of nitrogen functionalities are dependent on the nitrogen sources used and the pyrolysis temperature [17-19]. To increase the amount of N into CNT, other heteroatoms such as sulfur (S), boron (B) and phosphorus (P) can be added during the synthesis of NCNT [20-21]. Most studies reported that the ORR activity of the catalyst in alkaline media increases with the addition of S.

Among the nitrogen sources based polymer, polypyrrole (PPy) is the most extensively studied polymer for CNT catalyst due to its high conductivity, high surface area, flexible structure, facile synthesis and excellent environmental stability [22-23]. Furthermore, PPy comprised of nitrogen heterocyclic compound in its structure. While the optimum temperature for heat treatment of N-doped carbon materials is usually carried out between 700 and 1000 °C [24]. Besides, the ORR activity of N-doped carbons is much higher in alkaline media than in acidic media [14].

In this work, catalysts were synthesized by chemical oxidative polymerization using different composition of polypyrrole (PPy) as N sources and toluene sulfonic acid (TsOH) as S source, followed by high temperature heat treatment. The catalysts were characterized using several methods for morphological and chemical composition, and structure. The activities towards ORR in alkaline media were measured using cyclic voltammetry (CV) and rotating disk electrode (RDE).

2. Experiment

2.1. Materials

Multiwalled carbon nanotube (MWCNT, 90% carbon basis) was purchased from Sigma Aldrich and treated with nitric acid (purchased from R & M Chemicals). Pyrrole (Py) was purchased from Merck and used without distillation. Toluene-4- sulfonic acid (TsOH) monohydrate and Iron (III) chloride ($FeCl_3$) were purchased from Merck and used as dopant and oxidant, respectively. Methanol and Nafion (5 wt.% hydro-alcoholic solution) were purchased from Sigma Aldrich. Concentrated potassium hydroxide (KOH) and Isopropyl alcohol (IPA) were purchased from J. T. Baker and Merck, respectively. All aqueous solutions were prepared using deionized water.

2.2. Catalyst preparation

The catalysts were synthesized via *in situ* chemical oxidative polymerization and high temperature heat treatment. The catalysts were prepared by the following procedure. Firstly, carbon nanotube (CNT, Sigma-aldrich), which was treated with nitric acid, was weight and mixed with 100 ml deionized water and sonicated for 1 h. Then, 0.95 g of toluene sulphonic acid (TsOH) was added and stirrer for 15 min. After that, 1 ml of pyrrole was added and stirred for 45 min. Then, $FeCl_3$ (1.14 g) in 10 ml distilled water was slowly added and stirred for 1 h. The product was then filtrated, washed with double distilled water and methanol, and dried in a vacuum oven at 60 °C for 12 h to obtain the PPy modified carbon nanotube. Lastly, thermal treatment of the sample was performed in a tube furnace at 700 °C for an hour under nitrogen atmosphere.

2.3. Physico-chemical characterization

The morphology of the as-prepared catalyst samples was investigated using a field emission scanning electron microscope (FESEM, MERLIN COMPACT Zeiss 2013). The crystallographic structure of the catalyst samples was determined using X-ray diffraction (XRD, D8 Advance/Bruker/2009). XRD patterns of the catalysts were performed with scattering angle 2θ range 20-80^o using CuKα radiation having wavelength λ = 1.504Å. EVA software was used to determine the crystallographic phase associated with the peaks that appear in the XRD patterns. Raman spectroscopy was applied to characterize the structure of the catalysts. Raman spectra were recorded in air using HORIBA Jobin Yvon LabRAM HR 800 UV with a thermoelectrically cooled CCD detector and holographic super-Notch filter. The samples were excited with the 532 nm Ar line. The elemental surface compositions of the catalysts were investigated using X-ray photoelectron spectroscopy (XPS). The analysis was carried out using a high resolution Auger electron spectrometer with X-ray photoelectron spectrometer (AES-XPS), model Axis Ultra DLD/Kratos/2009 using Al Kα radiation. The obtained data were analyzed with CasaXPS 2.3.15 rev 1.3.

2.4. Electrochemical measurements

The electrocatalytic activity towards ORR of the catalyst samples were tested in a conventional three-electrode system using an Autolab PGSTAT128N potentiostat. A glassy carbon-type electrode, a Pt wire and an Ag/Cl were used as the working electrode, the counter electrode and reference electrode, respectively. Catalyst ink containing 5 mg catalyst, 0.5 ml distilled water, 0.5 ml isopropyl alcohol and 50 µl Nafion solution (5 wt %, Dupont) were ultrasonically mixed for 1 h. Then, 10 µl of catalyst ink was pippeted onto glassy electrode (0.1963 cm^2), and the electrode was dried in air at room temperature. The electrolyte in each experiment was deaerated with oxygen for 20 min, to prepare an oxygen saturated electrolyte. Cyclic voltammetry (CV) was recorded in the potential range of -1.0 to 0.0 V at a scan rate of 10 mV/s, and the RDE was recorded at rotation speeds of 400 rpm, 625 rpm, 900 rpm, 1225 rpm and 1600 rpm. All the CV and RDE measurements were performed in 0.1 mol/l KOH.

3. Results and discussions

Fig. 1 shows the XRD patterns of the pure CNT and NCNT catalyst. It can be observed that CNT and NCNT catalyst have similar structure. The diffraction peak of NCNT catalyst at 2θ of about 26°, 43°, 54.5°and 78° are attributed to the carbon structure and corresponding to the graphite structure (002), (100), (004), and (110) respectively [25]. Compared to pure CNT, the NCNT catalyst sample shows lower intensity peak at all diffraction especially at 26°. This indicates that the nitrogen from PPy-TsOH has been successfully doped into CNT. Fig. 2 shows the SEM image for NCNT catalyst. The morphologies of the catalyst are globular and tubular structures that indicate to the polypyrrole and MWCNT, respectively.

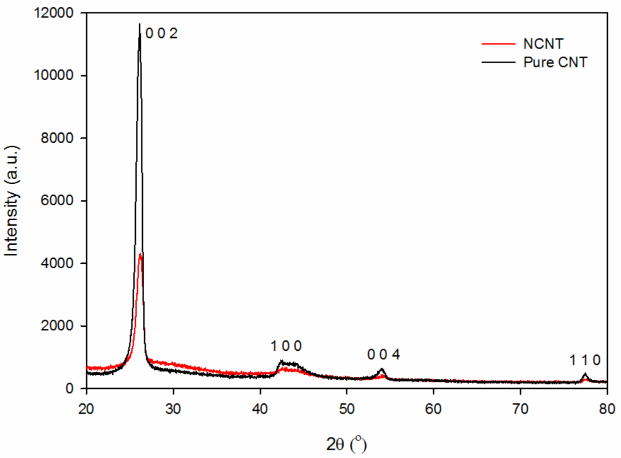


Fig. 1: XRD Patterns of CNT and NCNT

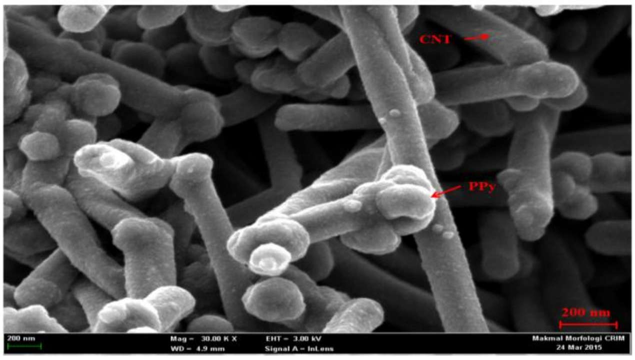


Fig. 2: SEM image of NCNT catalyst

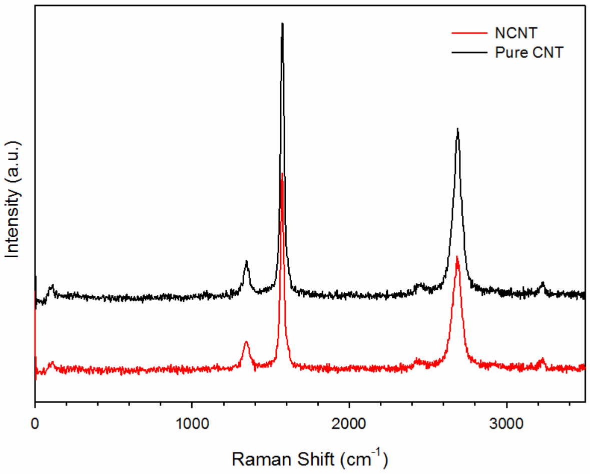


Fig. 3: Raman spectra of CNT and NCNT

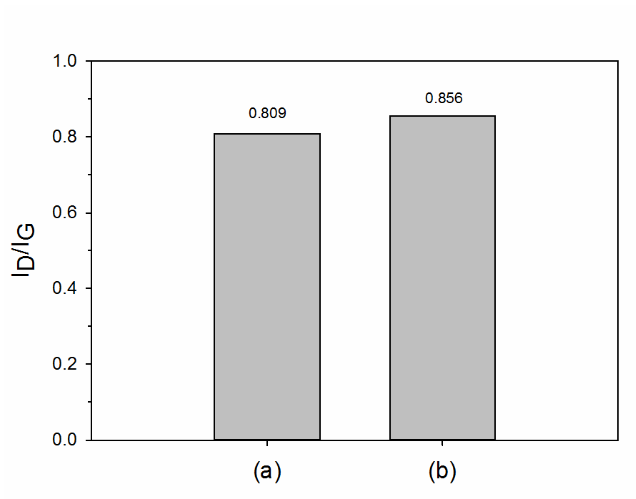


Fig. 4: I_D/I_G ratio of (a) CNT and (b) NCNT

Table 1: Peak of CNT and NCNT

Sample	D (cm^{-1})	I_D	G (cm^{-1})	I_G
CNT	1347	203	1576	251
NCNT	1344	202	1567	236

Raman spectroscopy is a powerful tool for identifying the structure, disorder, and doping of layer. Fig. 3 shows the Raman spectra of CNT and NCNT catalyst. It can be seen that CNT and NCT have different main peak as shows in Table 1. The amount of defects and the graphitic structure of CNT and NCNT catalyst can be estimated by determining the relative intensity of the D and G bands as shown in Fig. 4. The D band (disorder mode band) is related to the presence of the defects of nanotubes, while the G band is associated with the vibration of sp^2-bonded carbon atoms in a graphitic layer [26]. The information about the defect density of the graphite layer structure is given by the relative intensity ratio of the D and G bands (I_D/I_G). The defect structure increase as the I_D/I_G increases and therefore the degree of graphitization decreases. As shown in Table 1 and Fig. 4, the I_D/I_G ratio of NCNT is higher than pure CNT due to the coating process [27].

The N element bonding configuration for NCNT catalyst was further investigated by XPS analysis. The XPS survey spectrum of NCNT catalyst (Fig. 5a) shows the presence of atoms C (85.58%), N (10.06%), and O (4.36%). The XPS survey spectra for the NCNT catalyst exhibit a predominant C 1s peak at 287 eV and N 1s peak at 403 eV, confirmed the successful doping of N atoms into CNT. The C 1s spectrum of NCNT catalyst (Fig. 5b) can be described with four different signals at 287.3, 288.0, 289.3, and 292.1 eV, indicating the graphite-like sp^{2}C (36.78%), N-sp^{2}C (33.18%), N-sp^{3}C (14.48), and C-O type bond (15.57%), respectively [26]. The high resolution XPS spectrum of N 1s for NCNT catalyst (Fig. 5c) reveals the presence of four types of N configurations at 400.9, 402.2, 403.5, and 405.6 eV, which can be attributed to the N doping in the form of pyridinic-N (21.88%), pyrrolic-N (9.97%), graphitic-N (33.59%), and oxidized-N (34.74%) groups, respectively. In addition, the peak of O 1s (Fig. 5d) originated from C=O (533.2 eV) and C-OH or C-O-C (534.9 eV) which results from a possible formation of pyridine oxide (N^+-O^-) during the synthesis process [28-29].

The ORR activity of the catalyst was investigated by cyclic voltammetry (CV) in 0.1 M KOH. The measurements were performed in the potential range from 0.0 to -1.0 at scan rate 10 mV/s and measured in oxygen- and nitrogen-saturated electrolyte. The CV results are plotted in Fig. 6. The position of negative cathodic peak, $E_{p,c}$ is one of the criterion for ORR activity; the higher the ORR activity, the closer $E_{p,c}$ to the thermodynamic potential 1.17 V [29]. The onset potential, peak maximum, and current density and mass activity of the NCNT catalyst are -0.154 V vs. Ag/AgCl, -0.277 V vs. Ag/AgCl, and 0.455 mA cm^{-2}, respectively. In addition, a small peak of the NCNT catalyst can be observed at the potential of about -0.468 V vs. Ag/AgCl after the maximum reduction current density was reached. Additional active sites can be activated with rising over-potential leading to increasing reduction current.

The NCNT catalysts were also studied by RDE voltammetry in oxygen-saturated 0.1 M KOH at room temperature with the electrode rotating rates of 400, 625, 900, 1225 and 1600 rpm and potential scan rate of 10 mV/s. The RDE polarization curves of NCNT catalysts at different rotation rates are shown in Fig. 7. The ORR current density of each catalyst is increase with the electrode rotating speed, due to the faster mass transport. The RDE data can be used to calculate the electron transfer number (*n*) and the kinetic parameter.

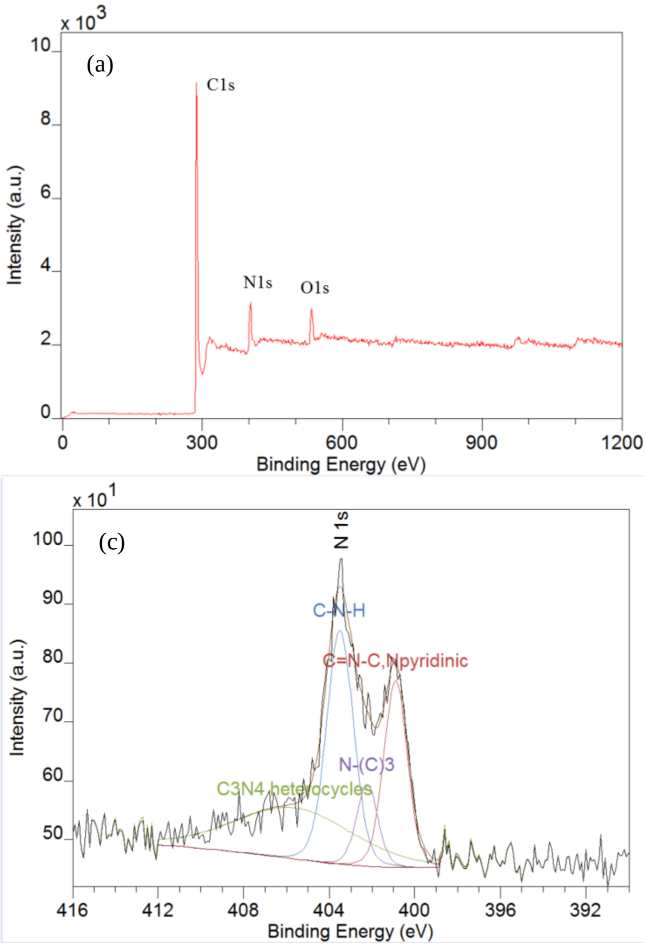
Based on RDE analysis, the electron transfer number (*n*) of the ORR can be calculated according to the Koutecky-Levich (K-L) equation [30]:

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{B\sqrt{\omega}}$$

Where *B* is the Levich slope which can be further defined as,

$$B=0.62nFAC_0D_0^{2/3}v^{-1/6}$$

Where *j* stands for the limiting disk current density, j_k is the kinetic limiting current density, *F* stands for Faraday constant (96.485 C mol^{-1}), *A* is the electrode area and ω is the angular frequency of rotation. The concentration of O_2 (C_0), the diffusion coefficient (D_0) of O_2 in 0.1 M KOH solution and the kinematic viscosity (v) of 0.1 M KOH solution are 1.15 x 10^{-6} mol cm^{-3}, 1.95 x 10^{-5} cm^2 s^{-1}, and 0.01 cm^2 s^{-1}, respectively.



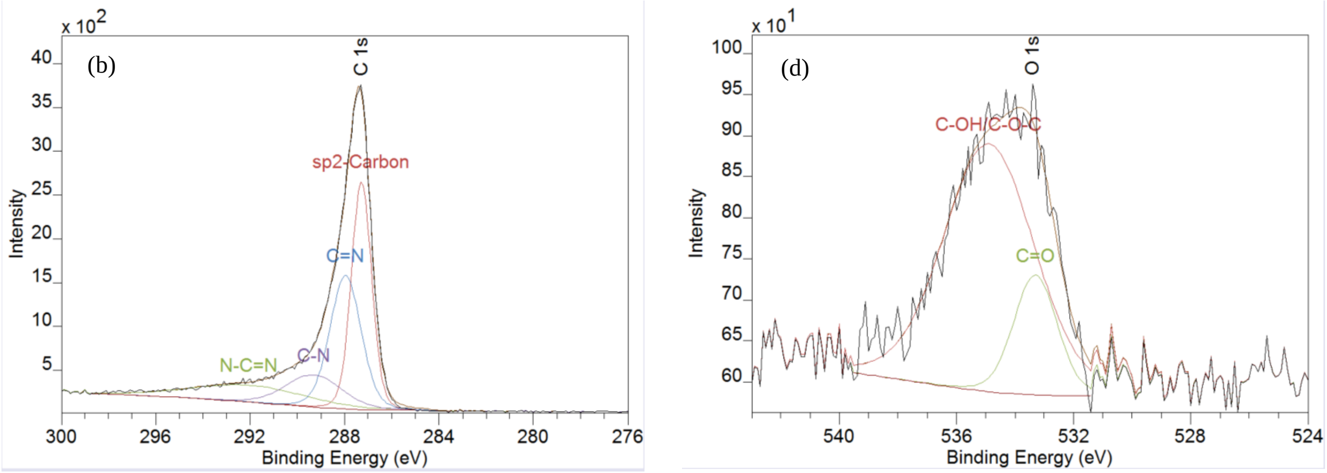


Fig. 5: XPS survey spectra of NCNT catalyst (a), High-resolution XPS of C 1s (b), N 1s (c) and O 1s (d)

Fig. 8 shows the K-L plots of NCNT catalysts at different potentials and rotation speeds. Based on Fig. 8, a linear relation was observed for j^{-1} and $\omega^{-1/2}$. The Levich slope of all the NCNT catalysts shows minor variation at applied potentials. Based on the Fig. 8, the electron transfer number (n) and the current density at potential 0.5 V vs. Ag/AgCl are 3.0 and 6.57, respectively. This indicated that the NCNT catalyst promoted the 4-electron oxygen reduction reaction. The Kotecky-Levich plots at different potential are not necessarily parallel. Parallelism and linearity of Koutecky-Levich plots at different potentials indicate that the number of transfer electron does not change in the given potential range. Fig. 8 shows that the slope of the curves changed as the potential changed; indicate that NCNT catalyst has different transfer electron number at different potential. This shows that the NCNT catalyst surface has various active sites with different activities [31].

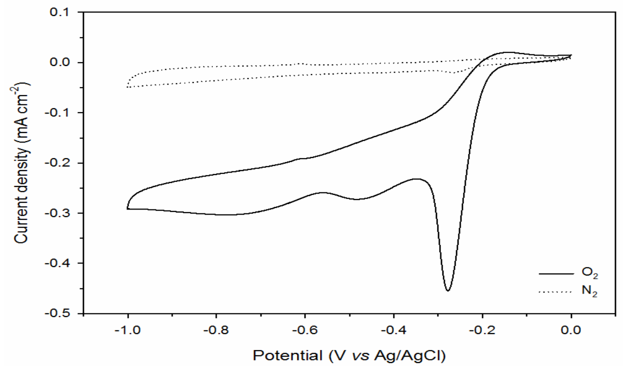


Fig. 6: CV curves of NCNT catalyst in O_2- and N_2-saturated 0.1 M KOH aqueous solution at scan rate of 10 mV s^{-1}

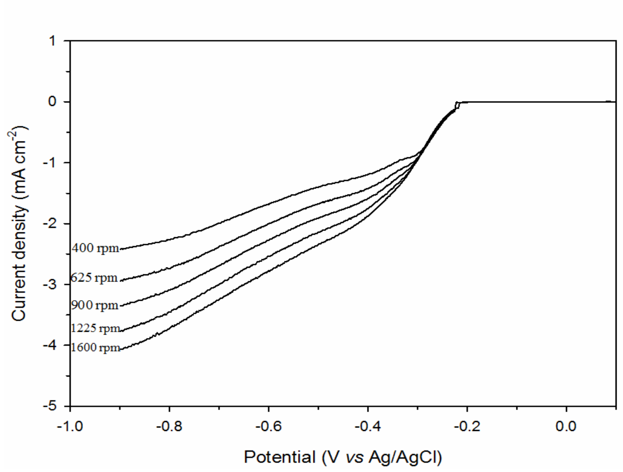


Fig. 7: RDE voltammograms of the NCNT catalyst at potential rate of 10 mV/s and various electrode rotating rates

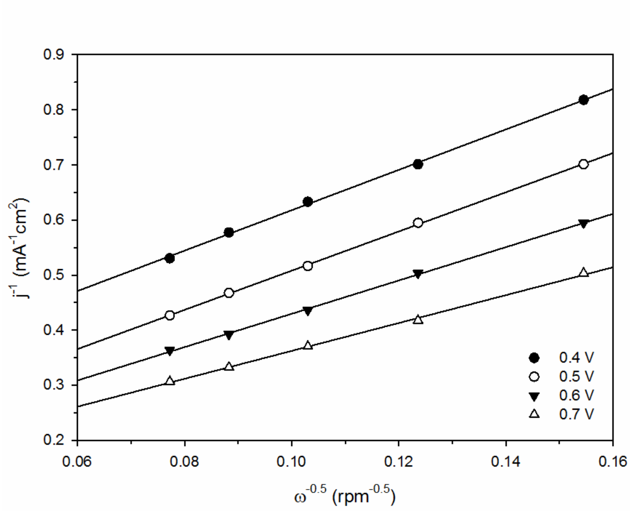


Fig. 8: Koutecky-Levich (K-L) plots of the NCNT catalyst

4. Conclusion

Nitrogen and polypyrrole/toluene sulfonic acid doped CNT was synthesized by chemical oxidative polymerization followed by high temperature heat treatment under N_2 atmosphere. The SEM studies showed that the morphologies of the catalysts are globular and tubular structure. The N atomic ratio in the near-surface region was found to be 10.06 % as derived from XPS measurements. The RDE studies revealed the NCNT catalyst promoted the 4-electron oxygen reduction reaction.

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