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# Electrocatalytic activity of iron and nickel phthalocyanines supported on multi-walled carbon nanotubes towards oxygen evolution reaction

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ABSTRACT

Non-noble metal catalysts for oxygen evolution were prepared by dispersing iron (II) phthalocyanine (FePc) and nickel (II) phthalocyanine (NiPc) on multi-walled carbon nanotubes (MWCNTs) which were used as high surface area support. The oxygen evolution reaction (OER) activity of those MWCNT-supported catalysts in alkaline and acidic solutions was studied by different electrochemical techniques such as cyclic voltamperometry, chronoamperometry (CA) and galvanostatic measurement. The developed hybrid catalysts showed better performance in basic solution and in this media NiPc/MWCNT catalyst had shown better OER performance than FePc/MWCNT. The electrodes were resistive to passivation and had reasonable stability. The obtained results suggest that the MWCNT support plays an important role on the catalytic properties towards the OER.

## 1. Introduction

All fossil fuels are nonrenewable, and as such they will eventually be depleted. Further, energy generation from fossil fuels require combustion, thus damaging the environment with pollutants and greenhouse gas emission. In order to sustain the future of the world with a clean environment and nondepletive energy resources, renewable energy is the obvious choice [1].

The splitting of water either electrochemically or photoelectrochemically by using of solar energy has the potential to provide a sustainable source of hydrogen for powering fuel cells, reducing $CO_2$ to fuels (e.g., $CH_4$, $CH_3OH$), and removing oxygen from biomass [2–4].While this process is well established, its energy efficiency is limited by the activities of the catalysts used at the anode and cathode. A particular challenge is to find highly active catalysts for the anodic oxidation of water, since the overpotential for this electrode is a major contributor to the inefficiency of splitting water electrochemically [5–7]. Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of anode materials, with the aim of achieving useful rates of the OER at the lowest possible overpotential, in order to optimise the overall electrolysis process [8–10]. While the oxides of Ru and Ir are considered to be the best OER catalysts for use in acid and base, respectively, these metals are among the rarest elements on earth and, hence, are expensive and are not practical for large-scale applications [11,12]. The oxides of first row transition metals, in particular nickel and cobalt, offer a compromise solution, although they possess inferior electrocatalytic activity for the OER. But the metal and metal oxides are suffering from corrosion effects especially in highly acidic and basic solutions and consequently have short life time.

Carbon electrodes modified with a variety of catalytic compounds are widely used in electrochemistry [13–16]. Metallophthalocyanine (MPc) are well known catalysts for many reactions and are known to lower overpotentials when employed as catalysts in electrochemical reactions. These catalysts are much cheaper than precious metallic catalysts and are commercially available. Nevertheless the use of MPc complexes as electrocatalysts for OER has received very little attention [17] and their electrocatalytic behaviour towards OER still needs to be improved to be of practical use. There are many reasons why these macromolecules lack the desired performance. One major reason is that, MPc molecules are prone to aggregation, which greatly decreases the active sites for OER. The other reason is that they do not have the proper interface to the carbon electrode material, so they cannot accept electrons efficiently. This is why several research groups have been focused on engineering a metal chelate catalyst into a good material that can interact efficiently with an electrode [18]. Recently, several reports have shown that MPc complexes integrated or supported on carbon nanotubes greatly enhance the electrocatalytic performance of the electrode [19–21]. The resulting metallophthalocyanine/CNT hybrid possesses the unique properties of phthalocyanine without any destruction of electronic properties and structures of CNTs [22]. CNTs actually provide a high

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surface area and electronic properties consistent with integration in an electrocatalytic device [23,24].

However, to the best of our knowledge, the use of such MPc–CNT hybrid for the OER is not reported in the literature so far. The aim of this paper is to evaluate the possibility of improving OER electrocatalytic activity of commercially available Ni and Fe phthalocyanines supported on multi-walled carbon nanotubes, in alkaline and acidic media. MPc complexes can easily adsorb on MWCNTs via non-covalent π–π interactions facilitating the electron transfer process and stabilizing the systems. MPc/MWCNTs hybrid catalysts were synthesized with a relatively simple method through direct mixing of FePc and NiPc and MWCNTs in tetrahydrofuran (THF) under ultrasonication.

Cyclic voltamperometry (CV), chronoamperometry (CA) and galvanostatic measurements were performed to explore the electrocatalytic activity of the hybrid catalysts towards the OER.

## 2. Experimental

### 2.1. Apparatus

Voltammetric studies were accomplished using a μ Autolab – type III. The software of this device was GPES version 4.9. A 780 Metrohm pH meter was used for pH measurements. The three-electrode system consists of bare or modified carbon paste electrode (CPE) as a working electrode, Ag|AgCl| 3 M KCl as a reference electrode and a Pt wire as a counter electrode were used. The body of the working electrode was a Teflon cylinder (2.0 mm i.d.), which was tightly packed with carbon paste. A stainless steel rod was inserted into the Teflon tube containing carbon paste to establish the electrical contact. All voltammetric experiments were performed at room temperature (25 ± 0.5 °C) in either 0.5 M $H_2SO_4$ or 0.1 M KOH solutions. All experiments were conducted under an $N_2$ atmosphere after degassing the solutions with highly pure $N_2$ for at least 15 min.

### 2.2. Material and solutions

All materials and reagents were analytical grade and used without further purification. Graphite fine powder (extra pure, particle size < 50 μm) was purchased from Merck. Nickel phthalocyanine and iron phthalocyanine were obtained from Aldrich and TCI respectively. THF and KOH were purchased from Merck and used as received. Nafion solution (0.5 wt% in alcohol) and paraffin oil were purchased from Fluka. $H_2SO_4$ was obtained from Panreac. Pristine MWCNT was purchased from Aldrich. All solutions were prepared with deionized water.

### 2.3. Electrode preparation

#### 2.3.1. Pretreatment of MWCNT

The pristine MWCNT (OD = 10–30 nm, ID = 5–10 nm, length = 0.5–500 μM, 95%) was purified and activated before use. For this purpose, MWCNT was stirred in 3:1 (v/v) $H_2SO_4/HNO_3$ solution mixture for 24 h and was then filtered and washed several times with deionized water for complete removal of acids. The resultant MWCNT was then dried at 80 °C in an oven overnight [25]. Acid treatment removes the amorphous carbon and metal oxide impurities and produces oxygen-containing moieties (for example carboxylic acid groups) at the open ends of the nanotubes which make it dispersible in aqueous media.

#### 2.3.2. Catalyst preparation

Catalyst was prepared as it is described elsewhere [26]. Briefly, MPcs were first dissolved in THF and their impregnation on pretreated MWCNTs was then performed as follows. A portion of MWCNT powder (MWCNTs/MPcs = 8, 7, 5, 3.5, 2 and 1, w/w) was added into the catalyst solution, followed by ultrasonication (20 min) to form a homogeneous dispersion. Then, the THF solvent was evaporated under a nitrogen stream. A schematic representation of these hybrid catalysts systems is suggested in Fig. 1.

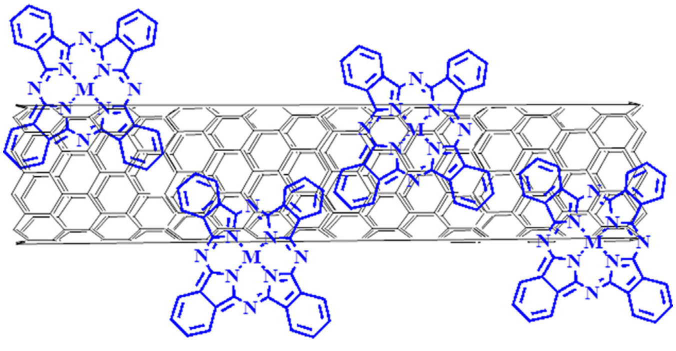

**Fig. 1.** Schematic representation of the hybrid catalysts (*M* = Fe or Ni).

Finally, 4 mg of resultant hybrid catalyst powders (FePc/MWCNTs or NiPc/MWCNTs) and 80 μl of 5 wt% Nafion solution were dispersed in 1 ml of 4:1 (v/v) water/ethanol by at least 30 min sonication to form a homogeneous catalyst ink.

Additionally MWCNT ink (without MPcs) was prepared by dispersing appropriate amount of pretreated MWCNT and 80 μl of 5 wt% Nafion in 1 ml of 4:1 (v/v) water/ethanol by at least 30 min sonication to form a homogeneous ink. The amount of MWCNT was chosen so that its quantity was equal to MWCNT in the hybrid catalyst ink after applying them on the CPE for modification purpose. Furthermore MPc inks (without MWCNT) were prepared by dispersing appropriate amount of MPcs and 80 μl of 5 wt% Nafion in 1 ml of 4:1 (v/v) water/ethanol by at least 30 min sonication to form a homogeneous ink. The amounts of MPcs were chosen so that their quantities were equal to MPcs in the hybrid catalyst ink after applying them on the CPE for modification purpose.

#### 2.3.3. Constructing the electrode

In the first step, carbon paste was prepared by mixing the graphite powder and paraffin oil (70:30, w/w) and a portion of the resulting paste was packed firmly into the cavity (2.0 mm diameter) of a Teflon tube. A stainless steel rod was inserted into the carbon paste (CP) in the tube for electrical connection. Surface of the electrodes was polished and smoothed with polishing paper.

Each active layer was deposited from each prepared inks (either hybrid catalyst ink or MPcs inks or MWCNT ink) by casting 5 μl onto the individual CPE and drying under air environment to create a smooth film. Moreover, for comparison, 5 μl of homogenous mixture solution of 5 wt% Nafion and 1 ml of 4:1 (v/v) water/ethanol was deposited on a CPE to serve as a bare electrode.

Before each experiment, the electrodes were first pretreated by several cycling between 0.0 and 0.5 V.

## 3. Results and discussion

### 3.1. Effect of MWCNTs:MPcs ratio

Different MWCNT:MPcs ratios were used for fabrication hybrid catalysts. Fig. 2(A) and (B) shows the effect of loading amount of MPcs on MWCNT on the electrocatalytic current density of OER in 0.5 $H_2SO_4$ and 0.1 M KOH solutions at 1.0 V vs. Ag/AgCl. Each data points were replicated 5 times and their standard deviation is exhibited by error bars. As these figures illustrate, at 7:1 ratio of MWCNT:FePc, this hybrid catalyst showed highest catalytic current density for OER in both acidic and basic media and MWCNT:NiPc