



# Electrocatalytic hydrogen peroxide formation on mesoporous non-metal nitrogen-doped carbon catalyst<sup>☆</sup>

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## ABSTRACT

Direct electrochemical formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) from pure O<sub>2</sub> and H<sub>2</sub> on cheap metal-free earth abundant catalysts has emerged as the highest atom-efficient and environmentally friendly reaction pathway and is therefore of great interest from an academic and industrial point of view. Very recently, novel metal-free mesoporous nitrogen-doped carbon catalysts have attracted large attention due to the unique reactivity and selectivity for the electrochemical hydrogen peroxide formation [1–3]. In this work, we provide deeper insights into the electrocatalytic activity, selectivity and durability of novel metal-free mesoporous nitrogen-doped carbon catalyst for the peroxide formation with a particular emphasis on the influence of experimental reaction parameters such as pH value and electrode potential for three different electrolytes. We used two independent approaches for the investigation of electrochemical hydrogen peroxide formation, namely rotating ring-disk electrode (RRDE) technique and photometric UV–VIS technique. Our electrochemical and photometric results clearly revealed a considerable peroxide formation activity as well as high catalyst durability for the metal-free nitrogen-doped carbon catalyst material in both acidic as well as neutral medium at the same electrode potential under ambient temperature and pressure. In addition, the obtained electrochemical reactivity and selectivity indicate that the mechanisms for the electrochemical formation and decomposition of peroxide are strongly dependent on the pH value and electrode potential.

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## 1. Introduction

Direct synthesis of chemicals from its pure elements or bi-molecules under ambient conditions often represents the most atomically-economic reaction route. The understanding of the elemental processes as well as the identification of all relevant experimental and intrinsic parameters and steps for many (electro) catalytic reactions are, however, highly complex and still poorly understood to date. The electrochemical direct conversion of pure hydrogen and oxygen to hydrogen peroxide is such a prominent example. Hydrogen peroxide is among one of the 100 most important chemicals in the world [4], because it is used in a lot of different fields of chemical and chemistry-related industries e.g. for pulp and paper bleaching, wastewater treatment or as “green” detergents and in different chemical syntheses [5]. Today, hydrogen peroxide is industrially produced via the anthraquinone process in

large-scale plants [6,7]. Alternative and “on the place of use” located production methods are also discussed in the literature e.g. membrane, fuel cell or plasma reactors [8–10].

In general, the reaction of pure hydrogen and oxygen leads to the formation of two main products, namely water and/or hydrogen peroxide. Since the direct conversion of hydrogen and oxygen is strongly exothermic, electrochemical membrane reactors, e.g. fuel cells, are typically employed to separate the two half-cell reactions; that are the hydrogen oxidation reaction [11,12] on the anode and the oxygen reduction reaction (ORR) on the cathode side [8,13,14]. From the perspective of the oxygen electroreduction, three reaction pathways are possible: (a) the direct two-electron process to generate H<sub>2</sub>O<sub>2</sub>, (b) the overall four-electron process consisting of H<sub>2</sub>O<sub>2</sub> formation followed by consecutive reductive decomposition of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O and finally (c) the direct four-electron process for the formation of H<sub>2</sub>O [15–17].

In fuel cell research, different cathode electrocatalyst concepts are discussed in terms of activity and stability for the efficient electrochemical conversion of oxygen. These concepts largely involve the utilization of metal nanoparticles dispersed on high surface area carbon support materials. The metal nanoparticles, such

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as pure platinum or platinum alloys with e.g. Cu, Co, Ni largely are the catalytically active reaction centers for the oxygen electroreduction. Improved ORR activities have been reported for dealloyed core-shell nanoparticle catalysts [18–23], Pt skin catalysts [24,25], Pt monolayer catalysts [26,27] or non-noble metal catalysts, e.g. Fe/Co/N/C or nitrogen-doped carbons [28–33]. Recently, pure nitrogen-doped carbon catalysts have attracted great attention due to their high performance for the electrochemical O<sub>2</sub> reduction toward H<sub>2</sub>O without usage of costly precious metals [34,35]. On the other side, only a handful of electrocatalyst concepts for the electrocatalytic hydrogen peroxide production are reported to date. Most of the H<sub>2</sub>O<sub>2</sub> electrocatalysts involve complexes (e.g. N-ligands like porphyrin or chlorin) containing metals like Fe, Pd or Co [36,37] and supported metal (e.g. Pd, Au-Pd, Pt-Hg, Pd-Hg) nanoparticles [2,36,38–44]. In comparison, typical Pt nanoparticle fuel cell catalysts, polycrystalline Pt and single crystals of Pt show a H<sub>2</sub>O<sub>2</sub> yield of less than 5% in acidic environment [22,45–47].

The long-term performance of electrocatalysts for the peroxide formation strongly suffers from the reaction conditions, such as aggressive H<sub>2</sub>O<sub>2</sub>-containing electrolyte, high potentials as well as from heat and pressure. For instance, the decomposition of peroxide leads to the release of OH· and OOH· radicals, resulting in an accelerated catalyst aging. A further challenge for the successful design of electrocatalysts is the selectivity toward H<sub>2</sub>O<sub>2</sub> at high yields. In particular, the series reaction of H<sub>2</sub>O<sub>2</sub> toward H<sub>2</sub>O via two-electron transfer should be largely eliminated.

Recent results of theoretical studies suggest, that hydrogen peroxide only shows physisorption to N-doped graphene and that the presence of protons facilitates O–O bond cleavage, i.e. peroxide reduction [48]. Inspired by investigations on the electron transfer process of mesoporous metal-free nitrogen-doped carbon catalyst using ionic liquid *N*-butyl-3-methylpyridinium dicyanamide (referred to as meso-BMP) in acidic and electrochemical environments, we have performed a comprehensive study on highly selective and active meso-BMP catalyst to highlight the influence of pH values and nature of electrolyte (acid–HClO<sub>4</sub>, alkaline–KOH and neutral–KClO<sub>4</sub>) for the electrochemical formation of H<sub>2</sub>O<sub>2</sub> using the rotating ring disk electrode (RRDE) technique. To support our electrochemical results in terms of activity, selectivity and durability for H<sub>2</sub>O<sub>2</sub> formation, we used additionally an independent photometric method to monitor the H<sub>2</sub>O<sub>2</sub> formation rate over the reaction time at a certain applied potential. We show that the H<sub>2</sub>O<sub>2</sub> formation rate is strongly influenced by the supporting electrolyte, pH values and applied voltage range. The observed difference in the reactivity-selectivity characteristics investigated on the meso-BMP catalyst is largely related to the pH dependent mechanisms and kinetics of the electrochemical H<sub>2</sub>O<sub>2</sub> formation. More importantly, the metal-free catalyst showed considerable stability during the long-term RRDE experiments, highlighting a high resistance of the active catalyst in the presence of preformed peroxide.

## 2. Experimental

All chemicals were used as received without further purification.

### 2.1. Synthesis of mesoporous nitrogen-doped carbon catalyst

Mesoporous nitrogen-doped carbon catalyst, referred to as meso-BMP, was synthesized using ionic liquids like *N*-butyl-3-methylpyridinium dicyanamide (BMP-dca, Ionic Liquide Technologies GmbH, Germany) followed by hard-templating using commercial silica nanoparticles (Ludox HS40).

### 2.2. Electrochemical measurement

All electrochemical measurements were conducted in a home-made three compartment electrochemical glass cell with a commercially available bipotentiostat (VSP-5, BioLogic, France) and a rotator (PINE Instruments, USA). The three electrode arrangement consisted of a Pt mesh as counter electrode, a reversible hydrogen electrode (Hydroflex HREF, Gaskatel, Germany) or mercury/mercury sulfate (AMETEK GmbH, Germany) as reference electrode and a glassy carbon electrode (PINE Instruments, USA, diameter 5 mm, 0.196 cm<sup>2</sup><sub>geo.</sub>) with a Pt ring (11 mm<sup>2</sup>) as working electrode. For thin catalyst film RRDE preparation, ~15 mg of catalyst powder was suspended in a mixture of 1.99 mL pure water (18 MOhm cm at room temperature, Satorious), 0.5 mL 2-propanol (Sigma-Aldrich) and 10 μL ionomer (Nafion solution, 5 wt%, Sigma-Aldrich). After horn sonification (Branson Sonifier 150D), an aliquot of 10 μL was pipetted onto the mirror-like polished and cleaned surface of a glassy carbon electrode and subsequently dried in air for 10 min at 60 °C. All measurements were conducted at room temperature.

### 2.3. Photometric peroxide measurement

The photometric peroxide investigations took place at 500 nm by utilization of a peroxide test kit (Merck, #118789) as described from the supplier. The voltage of the working electrode was 0.1 V versus RHE with 1600 rotation per minute in a continuously O<sub>2</sub> purged (~250 mL/min) electrolyte solution. The electrolyte was 0.1 M KOH (prepared by dissolving of solid KOH pastilles, Sigma-Aldrich), KClO<sub>4</sub> (prepared by dissolving of solid KClO<sub>4</sub> powder, Sigma-Aldrich) or HClO<sub>4</sub> (prepared by diluting from a 70% stock solution, Sigma-Aldrich) solution. The photometric investigation is described in the following: A small volume of electrolyte from the reaction solution was taken and neutralized. Subsequently, reagents as instructed for the commercial peroxide test (Merck, #118789) were added. The color of the solution changed from colorless and clear into green/yellow corresponding to the peroxide concentration. The colored sample was measured at 500 nm. According to the Lambert–Beer's law, which describes a linear behavior of concentration and absorption, a fresh calibration curve was established for each series of electrolyte measurements. The peroxide concentrations were subsequently determined based on the calibration curve.

## 3. Results and discussion

### 3.1. Metal-free mesoporous nitrogen-doped carbon catalyst

The metal-free mesoporous nitrogen-doped carbon (meso-BMP) catalyst was synthesized by pyrolysis of ionic liquids and contains a relatively high nitrogen content of around 17 wt% obtained from the element analysis. The nitrogen adsorption BET (Brunauer-Emmett-Teller) surface area of the meso-BMP is around 320 m<sup>2</sup>/g. The total pore volume derived from Non Localized Density Functional Theory (NLDFT) calculation is 0.749 cm<sup>3</sup>/g, with a mesopore volume of 0.09 cm<sup>3</sup>/g. It is noted that no metal was used or added during the synthesis. Element analysis, X-ray photoelectron spectroscopy (XPS) and cyclic voltammograms (Fig. S1) do not hint on any metals inside the meso-BMP material.

Fig. 1(a) shows a XPS spectrum of the meso-BMP catalyst. Based on the multi-peak fit analysis, the nitrogen N 1s signal indicates the presence of pyridinic (44% at 398.4 eV), pyrrolic (17% at 399.8 eV), graphitic (33% at 401.0 eV) and a few N-oxidic (6% at 402.9 eV) nitrogens. The theoretically predicted order of reactivity is pyridinic > quaternary > pristine graphene for the

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