



# Direct synthesis of Pt-free catalyst on gas diffusion layer of fuel cell and usage of high boiling point fuels for efficient utilization of waste heat



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## HIGHLIGHTS

- One-step direct synthesis of boron-doped carbon nanotubes (BCNTs) on gas diffusion layer (GDL).
- Home built fuel-cell testing using BCNTs on GDL as Pt-free cathode catalyst.
- BCNTs exhibit concentration dependent oxygen reduction reaction and the cell performance.
- Effective utilization of waste heat to raise the fuel temperature.
- Fuel selectivity to raise the fuel temperature and the overall performance of the fuel cells.

## ARTICLE INFO

### Keywords:

Doped carbon nanotubes  
Gas diffusion layer  
Electrocatalyst  
Oxygen reduction reaction  
Fuel cell  
Waste heat

## ABSTRACT

Gas diffusion layers (GDL) and electrocatalysts are integral parts of fuel cells. It is, however, a challenging task to grow Pt-free robust electrocatalyst directly on GDL for oxygen reduction reaction (ORR) – a key reaction in fuel cells. Here, we demonstrate that boron-doped carbon nanotubes (BCNTs) grown directly on gas-diffusion layer (which avoid the need of ionomer solution used for catalyst loading) can be used as efficient Pt-free catalyst in alcohol fuel cells. Increase in boron concentration improves the electrochemical ORR activity in terms of onset and ORR peak positions, half-wave potentials and diffusion-limited current density that ensure the optimization of the device performance. The preferential  $4e^-$  pathway, excellent cell performance, superior tolerance to fuel crossover and long-term stability makes directly grown BCNTs as an efficient Pt-free cathode catalyst for cost-effective fuel cells. The maximum power density of the fuel cell is found to increase monotonically with boron concentration. In addition to the application of BCNTs in fuel cell, we have introduced the concept of hot fuels so that waste heat can effectively be used and external power sources can be avoided. The fuel is passed through a hot bath for the realization of hot fuel which eventually increases the operating temperature of the cell (for example: 60 °C for methanol and 80 °C for ethyleneglycol, avoids the requirement of heating arrangement) and hence, the performance. Overall, different strategies to design ultimate fuel cells for their commercial adoption and effective utilization of waste heat have been outlined.

## 1. Introduction

Development of the eco-friendly sustainable energy resources in order to reduce the dependency on environmental offensive and traditional fossil fuel based energy resources, has motivated researchers around the globe [1–7]. In this regard, electrochemical energy conversion devices like polymer electrolyte fuel cells have potential to power the automotive as well as portable devices for future applications [1–7]. Though the theoretical efficiency is much higher than internal combustion engines, it is still far from reality and one of the main reasons is the sluggish/complex oxygen reduction reaction (ORR) at cathode. Generally, precious metal group (PMG) based catalysts have

been considered suitable to expedite ORR process [8–17]. However, the implementation of PMG based catalysts hinders the wide spread commercialization of the electrochemical devices due to their high cost, susceptibility towards operational stability above room temperature, poor fuel tolerance, etc. [8–17]. Therefore, quest is on to develop efficient and robust electrocatalysts that can replace PMG-based ORR catalysts [18–21]. Recently, hetero-atom doped carbon nanostructures [16,22–50] are shown to have the potential to replace Pt. For example, nitrogen doping modifies the local chemical reactivity of surrounding carbon atoms that facilitates the ORR activity. Other advantages associated with hetero-atom doped carbon nanostructures are excellent selectivity towards ORR activity and superior tolerance to alcohols that

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are used as fuels. Nitrogen-doped carbon nanostructures have been implemented [30,31,46] in fuel cells that shows better durability over state-of-the-art Pt as cathode catalyst. Alike to nitrogen, boron too has the potential to introduce the active sites by creating the charge and structural imbalance which facilitates the ORR activity [34–36,44].

In addition, gas-diffusion layer (GDL) also plays an important role and has the ability to influence the device performances. The basic functions of GDL include the transportation of the oxygen gas from the flow channel grooved in the bipolar plates to the electrocatalyst layer, and provides the conducting pathways for electrons with minimum resistance while keeping the polymer electrolyte membrane in a wet condition at low humidity to maintain high conductivity [51,52]. Generally, the catalyst is introduced by loading either on GDL (such as carbon paper or cloth) [30] or on electrolyte material [31] with the help of an ionomer solution that requires optimization for best cell performances [53]. In this regard, the direct growth of catalysts on the GDLs or electrolyte materials can avoid the use of resistive/expensive ionomer solution. It is not feasible to grow the carbon nanostructures directly on the electrolyte materials because of the requirement of high temperature, the possible growth on GDLs can be a possible approach. Moreover, the cell performance can be enhanced further by increasing the operating temperature. In general, the cells are heated to the operating temperature that employs a heating source while maintaining the supplied fuels at normal temperature and therefore, requires additional power consumption which further add up to the cost. To the best of our knowledge, no attempt has been made to use hot fuels. The advantage associated with the hot fuels is that the waste heat generated from portable electronic devices or internal combustion engines can be explored to increase the fuel temperature and hence, the performance of the cells without any additional heating arrangements.

We have made an attempt to address few challenges, as discussed above, associated with direct alcohol fuel cells (DAFCs) in order to achieve better operational efficiency. We employ a one-step pyrolysis route for direct large area facile synthesis of BCNTs on GDL with different boron concentration for ORR study followed by its application as Pt-free cathode catalyst in alkaline DAFC (ADAFC) as depicted in Scheme 1. We compared the ADAFC testing using BCNTs directly grown on GDL as well as the BCNTs pasted on GDL using nafion ionomer binder. The study suggests that the direct growth of catalyst on GDL provides an economic approach with good device performance. In addition, we report the effect of fuel temperature (hot fuel) rather than fuel cell temperature so that the concept of waste heat can effectively be utilized (Scheme 1). BCNTs exhibit good ORR activity in alkaline medium with practical durability and superior methanol tolerance. The ORR onset and half-wave potential along with current density increases with boron concentration which has been further substantiated by the increase in maximum power density ( $P_{max}$ ). With fuel temperature, the power density increases and one of the interesting observations is that the performance is found to depend on the boiling point of the fuel-water solution. Higher boiling point fuel such as ethylene glycol is

advantageous over methanol in this regard. Overall, our results provide different strategies to design efficient cost-effective fuel cells for their commercial adoption and effective utilization of waste heat to enhance the cell performance.

## 2. Experimental section

### 2.1. Materials

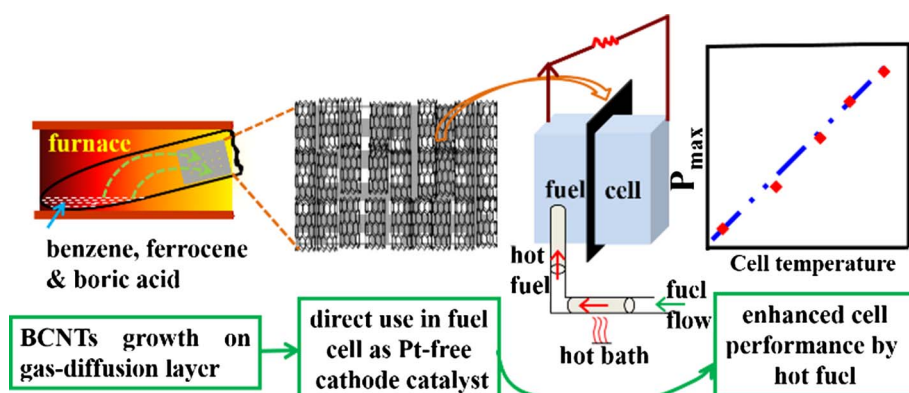
Ferrocene (Merck), benzene (S.D. Fine chemicals), boric acid (S.D. Fine chemicals) with 98, 99.7, 99.5% purity, respectively, and commercial carbon paper (Toray® Industries Inc.) are used for the direct growth of BCNTs on GDL (carbon paper). Commercial Pt/C (60% Pt loading, Arrora Matthey) is used without any further treatment. Nafion® membrane (117, Sigma Aldrich) [28,31] and Nafion® solution (5%, Sigma Aldrich) are used in fuel cells. Milli-Q (MQ) water is used for all the investigation.

### 2.2. Synthesis procedure of BCNTs

BCNTs with four different boron concentrations are synthesized by pyrolyzing benzene, ferrocene and boric acid in a Lenton tube furnace (LTF 14/-/180) [54]. In brief, 2 ml of benzene, 20 mg of ferrocene and different amount of boric acid are taken in a quartz tube and pyrolyzed at 950 °C for 3 h. Carbon paper (GDL) is inserted into the tube for CNT growth prior to the commencement of the experiment. The BCNTs synthesized with 50, 75, 100, and 125 mg of boric acid are denoted as BCNT1, BCNT2, BCNT3, and BCNT4, respectively. Similarly, pristine CNTs are synthesized by using ferrocene and benzene of the specified amounts under identical conditions without boric acid. For the electrochemical and fuel cell studies, the dimension of the carbon papers is taken to be  $5 \times 1$  and  $3 \times 3$  cm<sup>2</sup>, respectively.

### 2.3. Characterization

BCNTs are characterized by scanning electron microscopy (SEM, FEI SIRION), transmission electron microscopy (TEM, TECHNAI F30 from FEI), high resolution TEM (HRTEM, TECHNAI F30 from FEI), selected area electron diffraction (SAED, TECHNAI F30 from FEI), Raman spectroscopy (WITec, Germany, excitation wavelength of 532 nm), and X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD from Kratos). Cyclic voltammetry (CV), rotating-disk electrode (RDE, active area 0.07 cm<sup>2</sup>), and rotating ring-disk electrode (RRDE, active area 0.196 cm<sup>2</sup>) voltammetry are carried out in Gamry potentiostat/galvanostat (Reference 3000) and CHI instruments (700E), respectively. Fuel cell performance is tested with Electrochem Inc. (ECL 450™). The prepared BCNTs are gently scrapped of and dispersed in ethanol by ultrasonication followed by drop-casting on TEM grid. The grid is dried under lamp and vacuum desiccated for overnight to prepare the sample for TEM.



Scheme 1. From synthesis of BCNTs to fuel cells applications.

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