



# Palladium-nitrogen coordinated cobalt alloy towards hydrogen oxidation and oxygen reduction reactions with high catalytic activity in renewable energy generations of proton exchange membrane fuel cell



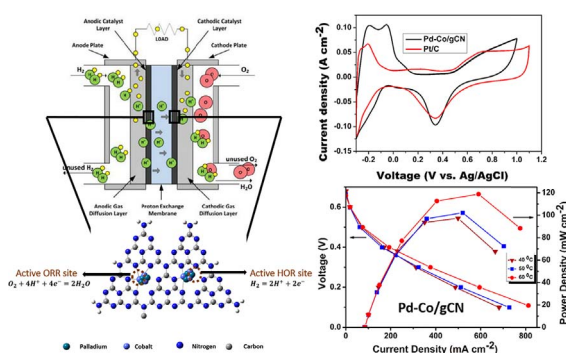
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## HIGHLIGHTS

- Pt free bimetallic electrocatalyst Pd-Co/gCN.
- Superior catalytic activity of Pd-Co/gCN in acidic medium for both ORR and HOR.
- TM-nitrogen complex acts as an active ORR site with elevated d band energy.
- Enhanced power density with completely platinum free single cell measurement.
- Pd-Co/gCN is a reliable replacement to conventional Pt/C for ORR energy conversion.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Oxygen reduction reaction (ORR) is one of the most important processes in energy conversion and conservation in proton exchange membrane fuel cell (PEMFC). In PEMFC, developing non-platinum based catalyst by understanding the catalytic activity for both oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) is essential for energy storage/conversion. Herein, we report preparation of such a bi-functional and durable catalyst consists of palladium and nitrogen coordinated cobalt and its catalytic activity is discussed methodically. Palladium cobalt bimetallic alloy nanoparticles dispersed over graphitic carbon nitride (Pd-Co/gCN) serves as an efficient anode and cathode catalyst in proton exchange membrane fuel cell for energy conversion. Incorporation of cobalt with palladium in nitrogen rich support material optimally modifies the bond strength of palladium-hydrogen (Pd-H) complex and promotes HOR, results in significant improvement of overpotential at the anode whereas, the nitrogen coordinated cobalt predominantly enhances the ORR activity at the cathode in acidic medium. Effects of mass transfer on the kinetics of ORR were investigated with rotating disc electrode (RDE). The hydrodynamic voltammograms were investigated to determine the kinetic parameters using the Koutecky–Levich equation. Our study presents an experimental realization of unveiling a good power density with high fuel utilization efficiency in a single cell for electrochemical energy conversion with complete elimination of platinum.

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## 1. Introduction

Proton exchange membrane fuel cell is considered as a promising high efficiency and low emission energy conversion device. The performance of this storage device is limited by the sluggish ORR reaction kinetics, which plays the crucial role to confine device performance in terms of power density as well as longevity [1]. Due to multi electron transfer process, the ORR experiences a slow reaction kinetics with a large overpotential. To address this issue platinum-based catalysts are needed in order to improve the reaction kinetics. But the cost and rarity of platinum (Pt) are the main obstacles towards commercialization of fuel cell technology. This situation triggered the exploration of non-platinum based, cost efficient durable electrocatalyst for the fuel cell. In proton exchange membrane fuel cell (PEMFC), for both hydrogen oxidation reaction (HOR) at anode and oxygen reduction reaction (ORR) at cathode platinum is known to be the most efficient electrocatalyst so far, which offers the lowest overpotential. Other than platinum, palladium (Pd) is known to have the catalytic activity comparable to platinum. High affinity for hydrogen makes Pd an appropriate replacement of Pt. Though the relative cost of Pd in comparison of Pt is almost half it is still above the acceptable levels for large-scale commercial application [2]. In this scenario, a various bimetallic alloy composed of palladium and transition metal (TM) attracted much attention not only because of the cost reduction but due to its excellent catalytic activity. Alloying TM with palladium optimally modifies the bond strength with adsorbents which gives rise to the enhanced catalytic activity compared to the Pd [3]. The bond strength of Pd-H<sub>ads</sub> is even stronger than Pt-H<sub>ads</sub>, resulting in sluggish reaction kinetics of H<sub>ads</sub> oxidation and eventually blocks the adsorption sites for other H<sub>2</sub> molecules [3]. Moreover, several groups have reported an enhancement in reaction kinetics with a reduction in the overpotential for ORR with Pd-Co bimetallic electrocatalyst via different thermodynamic modeling, assuming that increased activity of the alloy is because of the incorporation of active metals such as Co which results in ease of dissociation of the O<sub>2</sub> [4,5]. Additionally nitrogen enriched transition metal complex is a well reported active ORR site. So as Pd-Co alloy fulfils all the requirements necessary to be an efficient anode as well as a cathode catalyst for fuel cell, our aim was to fabricate a single catalyst for HOR and ORR with Pd-Co alloy dispersed over a suitable support material.

It has already been reported that nitrogen enriched carbon support materials not only possess outstanding catalytic activity towards ORR reaction but also are low cost, durable and environmental friendly [6–9]. Nitrogen-doped graphene has been studied in detail due to its excellent electrocatalytic activities as well as low cost and good durability. However, nitrogen doped graphene alone shows lower ORR activity in acidic solutions due to the limited catalytic activity of carbon nanomaterials, which still needs further improvement for practical applications, particularly for use in proton-exchange membrane (PEM) fuel cells. Some of the theoretical studies have already shown the incorporation of transition metal coordinated with the nitrogen atom (more specifically pyridinic and graphitic nitrogen) in the hexagonal framework of carbon drastically increases the ORR activity [10]. In this reference, carbon nitride is the ideal replacement of solely carbon based support materials. Among other phases of carbon nitride, the graphitic phase is the most stable allotrope [7]. This material gathered enormous attention in catalysis, energy conversion and storage because of its high nitrogen content which includes the pyridinic and graphitic species and maximum nitrogen content among all nitrogen enriched carbon materials [8].

Graphitic carbon nitride can be synthesized in numerous ways, which involves the thermal polycondensation of several cheap nitrogen-containing precursors in the air or inert atmosphere. Several kinds of literature reported two possible structures of polymeric gCN, which are s-triazine and tri-s-triazine based [7]. Density functional theory (DFT) calculations proved that the gCN system consists of the melon-based

species (i.e. tri-s-triazine) which are energetically more stable than the melamine-based species (i.e. s-triazine) [7,11]. The gCN has been verified as a superior support material for metal catalyst nanoparticles because of its excellent thermal and mechanical stability along with the anti corrosive nature in acidic and oxidative environments [8,12]. Along with these the presence of Lewis acid (the terminal and bridging NH– groups) and base sites (the lone pairs of electrons of N in triazine/heptazine rings) acts as an efficient anchoring site for metal nanoparticles [13].

Herein, based on the above considerations, for the first time, we designed and developed a novel bimetallic electrocatalyst dispersed on gCN (Pd-Co/gCN) and probed the catalytic activity of the bimetallic electrocatalyst towards HOR as well as ORR energy conversion. By exploring rotating disk electrode (RDE) and cyclic voltammetry studies on Pd-Co/gCN, the interactions between the electrocatalyst and the fuel via Co-N complexes which act as an active ORR center have been investigated. The unique structure due to the formation of Co-N complexes acts as an active ORR center and as a result, exhibits high ORR and HOR activity. Besides, in this study, for the first time the catalyst was used for the full cell polarization measurement, which resulted in the enhanced performance. To the best of our knowledge, there are no reports available on utilizing non-Pt for both cathode and anode as electrocatalysts for PEMFC energy conversion reactions. The present results show that Pd-Co/gCN electrocatalyst, synthesized using inexpensive materials, is a very potent energy conversion non-precious metal catalyst. Furthermore, with the outstanding electrochemical performance for ORR and HOR energy conversion in PEMFC, non-noble catalyst Pd-Co/gCN can be considered to be the replacement of the commercial Pt/C in energy conversion and storage devices.

## 2. Experimental

### 2.1. Materials

Melamine powder (Himedia) and palladium (II) chloride (Rankem) used were of analytical grade. Cobalt (II) chloride hexahydrate, ethylene glycol (EG), isopropyl alcohol (IPA) and sodium hydroxide pellets were delivered by Merck. Commercial Pt/C (Platinum on high surface area carbon) with 46.5 wt% Pt loading was purchased from Tanaka. Nafion 212 was supplied by Dupont. All chemicals were used as received without further purification. Deionized (DI) water from Millipore was used for all the synthesis.

### 2.2. Materials synthesis

Graphitic Carbon Nitride (gCN) was prepared by thermal condensation of nitrogen rich precursor melamine. Well ground melamine was taken in quartz boat inside a quartz tube and placed it in the middle of a horizontal tubular furnace. In an air atmosphere, the furnace was heated up to 600 °C for half an hour and allowed it to cool down to room temperature. After this whole process pale yellow powder was collected from the boat and labeled as gCN. Metal dispersion over gCN was achieved by well-known ethylene glycol reduction method (polyol reduction). The required amount of gCN was dispersed in 100 ml solution of EG and DI water (2:1) by ultra-sonication followed by stirring for 6 h. The calculated amount of PdCl<sub>2</sub> and CoCl<sub>2</sub> were first dispersed in 50 ml of the above-mentioned solution then added to the dispersed gCN in drop wise manner. The final solution was continuously stirred for 12 h. After making the pH 11 by adding 1(M) NaOH solution slowly the solution was refluxed for 8 h. Amount of the precursor salts were calculated in such a way that Pd:Co ratio in the electrocatalyst was 3:1. The final product was filtered and vacuum dried at 60 °C for 6 h and labeled as Pd-Co/g-CN. For comparison, another catalyst Pd/g-CN was prepared by following the same procedure mentioned above. Pd loading kept same for both the catalysts.

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