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Surfactant assisted synthesis of Pt-Pd/MWCNT and evaluation as cathode catalyst for proton exchange membrane fuel cell

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ABSTRACT

This study evaluates the role of two types of surfactants, the anionic sodium dodecyl sulfate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) on the synthesis and properties of multi-walled carbon nanotube (MWCNT) supported bi-metallic Pt-Pd (atomic ratio 1:1) nanoparticles (NPs) and assess their performance as cathode catalyst in proton exchange membrane fuel cell (PEMFC). Pt-Pd/CNT catalysts are prepared through microwave assisted, polyol route in presence of SDS (Pt-Pd/CNT-S) or CTAB (Pt-Pd/CNT-C) and their performance is compared with Pt-Pd/CNT prepared in an identical way without any surfactant. The study shows the prominent influence of the type of surfactant in disaggregation of MWCNT bundles and the dispersion of Pt-Pd NPs on MWCNT support, which in turn controls their catalytic activity for oxygen reduction reaction. In-situ electrochemical characterization studies show improvement in the catalytic activity of Pt-Pd/CNT-S compared to Pt-Pd/CNT-C and Pt-Pd/CNT, demonstrating SDS as an efficient disperser for MWCNT. High fuel cell performance achieved with Pt-Pd/CNT-S having less Pt content (~12 wt %) than the commonly employed pure Pt or Pt/C (20 wt %) catalysts demonstrates that it is a potential cathode catalyst for PEMFC that can help its wider commercialization.

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Introduction

Proton exchange membrane fuel cell (PEMFC) has been identified as an emerging sustainable energy source that can cater to efficient and green energy requirements of the society [1,2]. Currently, the commercial application of PEMFC is limited, largely due to its high cost originating from the usage of precious Pt catalyst for the electrochemical reactions at the electrodes [3]. Also, the slothful oxygen reduction reaction (ORR) kinetics occurring at the cathode necessitates a substantially higher Pt metal loading at the cathode compared to the anode, and contributes to increasing the cost further [4].

The useful strategies that can address these limitations are to decrease the loading of the expensive Pt metal in the catalyst along with increase in the ORR activity. This can be successfully achieved through alloying of pure Pt with a second metallic element M (M = transition metal) [5,6]. In this regard, Pd has attracted considerable attention as a highly suitable transition metal to alloy with Pt due to their similar lattice structure (face centered cubic) with a negligible lattice mismatch (of only 0.77%) along with a good miscibility which favor facile formation of bimetallic Pt-Pd nanostructures [7–9]. Besides, the cost of Pd is much lower compared to Pt (about one-third only).

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It is essential to disperse the metal nanoparticles (NPs) on suitable supports to achieve enhanced catalytic activity and stability of Pt based bi-metallic catalysts [10]. Carbonaceous materials, typically carbon blacks (CBs) are widely employed as support materials for state-of-art fuel cell electrocatalysts [11,12]. However, CBs are prone to electrochemical oxidation under fuel cell operating conditions, particularly during start up-shut down cycles [13]. Moreover, they suffer from significant mass transport limitations owing to their dense microporous structures which ultimately leads to low Pt utilization [14]. Under this context, multi-walled carbon nanotube (MWCNT) with excellent electronic conductivity, corrosion resistance and presence of inherent defective structures is a highly suitable carbonaceous support that can facilitate the nucleation, growth and dispersion of metal NPs for producing functional hybrid nanostructures [15,16]. Such hybrid nanostructures facilitate the availability of the active catalytic sites and also aid towards efficient mass transport of the reactants to the active sites which enhance the performance of the catalysts [17].

Most recently, comparative studies with different carbon support materials viz. CB, single-walled carbon nanotube, MWCNT and graphene, demonstrated superior fuel cell performance with MWCNT supported catalyst [18]. The enhanced performance was attributed to effective Pt utilization with MWCNT support. Similarly, Esmailifar et al. showed higher cell voltage at higher current densities with MWCNT supported catalyst as compared to standard, Pt/C catalyst [19]. The improved fuel cell performance was attributed to better mass transport of reactants and products with Pt/MWCNT cathode catalyst. With respect to durability of cathode catalysts in PEMFC, Liu et al. demonstrated exceptionally stable electrochemically active surface area for MWCNT supported catalyst than that of Pt/C [20]. Despite the inherent advantages associated with MWCNT for application as support materials in PEMFC, the useful retention of MWCNT properties in a composite structure comprising of metal NPs on MWCNT is highly dependent on the disaggregation and uniform dispersion of MWCNTs which allows effective utilization of composite properties towards catalysis [21,22]. A major obstacle towards realization of such a highly desirable NP/MWCNT composite is the aggregation of MWCNTs into bundles because of the van der Waal's forces which resist proper dispersion of MWCNTs in most aqueous media [23].

Covalent and non-covalent approaches are typically made use of for dispersing carbon nanotubes (CNTs) in the reaction media [24,25]. In the covalent chemical approach, effective functionalization of CNTs is achieved by the introduction of polar groups which results in improved dispersion in aqueous media and also acts as sites for metal NPs anchorage. In the work of Hsieh et al. chemical oxidation of MWCNTs with HNO_3 was carried out to implant surface oxide species [26]. The surface functional groups on the defect sites of MWCNTs act as sites of metal deposition and result in effective dispersion of metal NPs. Similarly, to facilitate the anchoring of metal NPs, Rosado et al. functionalized the surface of MWCNTs in a four stage process utilizing H_2O_2 and HNO_3 as oxidizing agents [27]. It is to be noted that though covalent approaches are effective in dispersion of MWCNTs and consequently metal NPs, the increase in dispersibility is attained at the cost of their

mechanical and electrical properties along with severe damage to the structure of CNTs [24,28,29].

On the other hand, in the non-covalent approach, the electrostatic interactions of surfactants are utilized to surmount the van der Waal's interaction of CNTs to achieve improved dispersibility. Through this route, effective dispersion of CNTs is achieved without affecting their chemical structure along with useful retention of the nanotube structure and property making non covalent approach highly attractive for attaining hybrid nanostructures [30]. The non-covalent modification of CNTs is generally realized using surfactants because of their easy availability, lower cost, lower toxicity, and facile experimental methods [31,32]. Zhang et al. utilized sodium dodecyl sulfate (SDS) as a dispersing agent for pristine and purified MWCNTs and concluded SDS as an efficient disperser for MWCNT [33]. However, no characteristic influence of SDS on the electrocatalytic properties of MWCNT-SDS modified glassy carbon (GC) electrode was evidenced. Kruusenberg et al. studied the influence of various surfactants: dihexadecyl hydrogen phosphate, cetyltrimethylammonium bromide (CTAB), SDS and Triton X-100 and investigated ORR activity of the surfactant modified GC electrode [34]. The study conducted in half cell mode with liquid electrolytes showed only marginal influence of surfactant on ORR catalytic activity. In spite of the remarkable potential of surfactant to tailor the electrochemical response of MWCNTs, the effect of surfactant on electrochemical properties of MWCNT supported metal NPs composite catalysts has not been thoroughly investigated. Moreover, there is not much information regarding influence of surfactant on ORR activity of MWCNT supported Pt based catalysts in PEMFC in the available literature. Hence, it is of interest to investigate the influence of surfactant on the ORR catalytic activity of MWCNT supported catalysts in PEMFC.

The aim of this work is to synthesize the composite, bimetallic Pt-Pd catalyst supported on MWCNT, via surfactant assisted route and to study the influence of surfactants on physicochemical properties and ORR activity of the catalyst. Two types of surfactants, the anionic SDS and cationic CTAB are employed to disperse MWCNT in the aqueous phase. The dispersing ability of the surfactant in synthesizing the nano-composite (Pt-Pd/CNT) catalysts and their resultant physicochemical and morphological characteristics are studied in comparison with that of the catalyst synthesized without any surfactant. Besides, ORR activity of the catalysts are investigated in detail in a working PEMFC. To the best of our knowledge, this study reports for the first time the prominent role played by the nature of surfactant on the synthesis of MWCNT supported bimetallic Pt-Pd catalyst and its ORR activity in PEMFC.

Experimental

Materials

K_2PtCl_6 and PdCl_2 were purchased from Alfa Aesar, India, whereas MWCNT is in-house product with surface area of $50\text{--}60\text{ m}^2\text{g}^{-1}$. SDS (Purity $\geq 99.0\%$) and CTAB (Purity $> 98\%$) was purchased from Sigma-Aldrich, India and ethylene glycol (EG,

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