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Short Communication

Iron and nitrogen co-doped titania framework as hybrid catalyst support for improved durability in polymer electrolyte fuel cells

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ABSTRACT

Stable hybrid support for platinum is prepared for polymer electrolyte fuel cells (PEFCs). The synergetic interaction between platinum and optimum level of iron and nitrogen co-doped into titania (TiON–Fe) framework moiety leads to superior cell performance and long-term stability as compared to platinum on carbon. Pt metal nanoparticles are deposited on TiON–Fe framework by colloidal method. Accelerated durability test (ADT) are performed for both Pt/C and Pt/TiON–Fe framework by potential hold at 1.2 V. The corrosion stability is increased for platinum deposited on TiON–Fe framework in PEFC and retains 50% of cell performance even after 200 h as compared to Pt/C with only 18% of cell performance for 80 h. The degradation of catalyst and loss of cell performance are explained by various characterizations before and after ADT.

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Introduction

The quest for an efficient and durable electrocatalyst for the generation of power from low temperature polymer electrolyte fuel cells (PEFCs) has led to the development of platinum (Pt) on alternative supports. In the past decade, Pt on carbon support (Pt/C) was widely used as electrocatalyst for oxygen reduction reaction in PEFC to improve the cell performance. However certain drawbacks such as carbon corrosion, metal agglomeration, metal detachment and dissolution, humidification and water management significantly affect fuel cell performance [1,2]. In the past, different literature reports

show that Pt deposition on various high surface area carbon supports such as carbon black, Kedjenblack, N-doped carbon etc., have improved ORR activity [3,4]. However, challenges are associated with its long term durability and steady-state PEFC performance. In addition, Pt supported on carbon nanotubes (CNTs), graphene and carbon nanofiber (CNFs) has shown considerable improvement in performance and durability even though they are cost intensive as against Pt/C [5–8].

In view of these constraints, in recent years focus is directed towards several metal oxide system as catalyst-support for PEFCs [9]. Certain non-precious metal based oxides of the form AO_2 , ABO_3 etc., have also been projected as

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prospective ORR electrocatalysts [10–12]. Especially, titania (TiO_2) is a better support for Pt which offers electron transport for ORR to improve the cell performance in spite of its increased Ohmic resistance [10,11]. However, Pt distribution and accessibility on TiO_2 being lesser than carbon support remains a main drawback [10]. As a result, there have been considerable studies to modify the surface and structural properties of TiO_2 , which improves the ORR activity and long-term durability [13,14]. Our earlier studies reported that, Pt on nitrogen doped TiO_2 (TiON) exhibits more corrosion resistance even after 50,000 cycles as compared to Pt/C [15].

In this communication, we report new hybrid catalyst support comprising iron (Fe) and nitrogen (N) co-doped titania (TiON–Fe) framework for Pt catalyst which may lead to larger electron donor state near the Fermi level and create more active sites for improved ORR activity. Optimization of Fe and N content in Pt supported on TiON–Fe framework indicate that Fe content of 1.5–2 wt.% and N content of 8–10 wt.% with respect to titania, showed excellent activity towards ORR [16]. The incorporation of Fe and N atoms on titania framework can particularly facilitate the ORR due to the creation of more disordered and defect sites on the support, and these are known to act as active sites for the ORR. The TiON–Fe framework can also change the charge distribution resulting in better interaction with Pt. The TiON–Fe framework also stabilizes Pt nanoparticles, improves long term fuel cell performance and retains the significant long term durability is experimentally demonstrated. The characterization of catalyst support material, fuel cell performance and fuel cell durability is described in the present work.

Experimental method

Titania is synthesized by hydrothermal method. Nitrogen and iron doping is carried out with melamine and ferric nitrate as N and Fe precursors respectively followed by heat treatment. 40 wt.% of Pt metal nanoparticles were deposited on TiON–Fe using colloidal method. The details of the experimental method and characterization techniques are given as Supporting information (ESI).

Results and discussion

The Powder X-ray diffraction (XRD) pattern of un-doped TiO_2 and TiON–Fe displayed sharp reflections at 27.5° matching with (110) lattice plane of tetragonal rutile TiO_2 framework (JCPDS 89-4202) shown in Fig. 1(a). A small shift is observed in the sample compared to un-doped TiO_2 . Fig. 1(a) XRD refinement clearly shows the change in c-axis (2.961 Å) during doping of Fe and N into TiO_2 framework as compared to un-doped TiO_2 (2.951 Å). The XRD patterns of Pt deposited on TiON–Fe and carbon are shown in Fig. 1(a). The peaks at 39.98 , 46.42 and 67.82° corresponds to (111), (200) and (220) planes that are characteristic of a face-centered cubic structure of Pt as confirmed from JCPDS # 87-0647.

The morphology of TiON–Fe and Pt-deposited on TiON–Fe were characterized by high resolution scanning electron microscopy (HR-SEM) and transmission electron microscopy

(TEM). The HR-SEM images of TiON–Fe reveal the nearly spherical microstructure with particle sizes varying between 50 and 400 nm as shown in Fig. 1(b). The overall distribution of smaller sized Pt particles on TiON–Fe is shown in Fig. 1(c). In addition, the individual elements present in Pt/TiON–Fe are confirmed from elemental mapping analysis given in Fig. 1(d). The EDAX results of TiON–Fe clearly show that, Fe and N are present 1.5–2 and 8–10 wt.% with respect to titania. However, small amounts of carbon (2–4 wt.%) are also observed which may be doped into TiO_2 site or on the surface of TiON–Fe framework (Fig. 2S, ESI). The TEM micrographs show the distribution of Pt nanoparticles to be moderately uniform with slight agglomeration over the both supports as shown in Figs. 3S and 4S (ESI). The Pt particle size derived from TEM images in both the supports are in good agreement with that measured from XRD.

In addition, to confirm the oxidation states of different elements present in Pt/C and Pt/TiON–Fe, photoelectron spectroscopy (XPS) measurements were carried out. The XPS survey spectrum of Pt/C and Pt/TiON–Fe shows predominant peaks corresponding to C and Pt in the former and N, Fe, Ti, O and Pt in the latter (Fig. 5S, ESI). Fig. 2(a) shows the deconvoluted peak of Ti 2p core level spectrum containing two main peaks Ti 2p_{3/2} and 2p_{1/2} at 459.1 and 465 eV corresponds to Ti (+4) oxidation state of TiON–Fe framework. Fig. 2(b) deconvoluted pattern of Fe 2p core level spectrum shows Fe 2p_{3/2} and 2p_{1/2} peaks with binding energies of 710.9 and 724.6 eV respectively corresponding to Fe (+3) oxidation state [17]. Similarly, Fig. 2(c) shows N 1s binding energy level of four different characteristic deconvoluted peaks namely N1, N2, N3 and N4. The N1 and N2 at 397.3 and 398.7 eV corresponds to N in Ti lattice (TiN) and C–N bond or N_2 groups adsorbed on the surface [17,18]. Similarly, N3 and N4 peak at 399.6 and 400.7 eV is allocated to O–Ti–N bond and Ti–O–N or Ti–N–O bond [17,19]. These peaks were not detected for Pt/ TiO_2 electrocatalyst in our previous work [15]. Fig. 2(d) represents three overlapping XPS peaks centred at 530.4 and 531.6 and 532.7 eV. The peak at 530.4 and 531.6 eV is related to the lattice oxygen Ti–O–Ti linkages and surface adsorbed hydroxyl groups. The other peak at 532.7 eV is assigned to oxygen in molecular water [15,16].

The Pt 4f core level peaks are observed for both Pt/TiON–Fe and Pt/C. It is clear from Fig. 2(e–f) that majority of Pt is present in metallic state (Pt^0) in both the materials. In addition, both materials also show a small percentage of Pt in Pt (+2) and Pt (+4) oxidation states. However, in the Pt/TiON–Fe, the peaks show a small shift compared to Pt/C. The 2p spectrum of Ti and Fe in Fe–TiON show that Ti is mostly present as Ti (+4) and Fe as Fe (+3) oxidation state. The Fe (+3) ensues to create the additional oxygen vacancy defects due to substitution of Ti (+4) by Fe (+3) in the TiO_2 lattice. The above replacement may cause a change in the charge distribution on TiO_2 matrix. In addition, XPS spectra for C is provided along with detailed discussions in Supporting information (Fig. 6S, ESI).

The comparative steady-state cell polarization for optimized Pt/TiON–Fe and Pt/C as cathode electrocatalysts in PEFC with Nafion-212 as proton conducting membrane and oxygen as the oxidant is shown in Fig. 3(a). PEFCs with Pt/TiON–Fe delivers a current density of 830 mA cm^{-2} at 0.6 V and a peak power density of 620 mW cm^{-2} as compared to a

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