



Synergy among manganese, nitrogen and carbon to improve the catalytic activity for oxygen reduction reaction



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HIGHLIGHTS

- Mn-N dual doped carbon, e.g. Mn-CN_x, was prepared.
- Mn-CN_x showed good catalytic activity for oxygen reduction reaction.
- Synergy among Mn, N and C results in the enhanced activity of Mn-CN_x.

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ABSTRACT

A highly active electrocatalyst for oxygen reduction reaction, manganese modified glycine derivative-carbon (Mn-CN_x), is synthesized by a two-step carbonizing process. X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy are used to characterize structure and morphology of the catalysts. Electrochemical tests show that Mn-CN_x has higher catalytic activity for oxygen reduction reaction than CN_x derived glycine and Mn modified Vulcan carbon. Moreover, the half-wave potential of Mn-CN_x is only 12 mV lower than that of commercial Pt/C. Mn-CN_x also has excellent durability to methanol crossover in alkaline solution, and thus provides a promising low cost, non-precious metal cathode catalyst for fuel cells.

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1. Introduction

The oxygen reduction reaction (ORR) is the dominant factor affecting the overall performance of proton exchange fuel cells (PEMFCs) as it is kinetically the slowest process [1–4]. In order to accelerate the ORR, high loadings of platinum are required on the cathode, which make PEMFCs too expensive for competitive commercialization [5,6]. Besides the high cost of Pt, the Pt-based electrocatalysts still face a series of challenges, such as low selectivity and poor durability [7]. Therefore, development of platinum-free [8,9], non-noble metal catalysts [10–12] and metal-free catalysts [13–17] which could be more efficient, durable, and less expensive than Pt-based catalysts has attracted much attention [18].

Among these Pt-free catalysts, nitrogen-doped carbon materials are attractive as potential ORR catalysts because they not only exhibit excellent electrocatalytic ORR activity but also have advantages, such as low cost, long durability, and environmental friendliness [13,15,16,19–21]. In particular, the pyridinic-N and graphitic-N type of nitrogen-doped carbon are quite active in ORR [22]. In pyridinic-N and graphitic-N, nitrogen atoms bond to two carbon atoms at the edges of the graphite planes, and with the three carbon atoms within the graphite (basal) plane. Nitrogen donates an electron from its electron pair to the π -conjugated bond system, imparting Lewis basic sites to the carbon and enabling the carbon to adsorb molecular oxygen and then transfer this electron to molecular oxygen to form intermediates, such as OH⁻, O₂, and HO₂⁻ [23–25]. However, while nitrogen clearly plays an important role in ORR on nitrogen-doped carbons materials, the ORR activity of most N-doped carbons is still not competitive to Pt-based catalysts.

In the last century, it has been reported that the alloys between Pt and Mn had better catalytic activity for ORR than Pt/C due to the

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electronic and geometric factors [26]. Kang et al. prepared cubic PtMn nanocrystals and studied its activity for ORR [27]. The MnPt nanocubes show higher ORR activity than the commercial catalyst in acid solution. Recently, the effect of Mn addition on the promotion of ORR activity of PtCo/C catalyst was also studied [28]. Furthermore, Jia et al. studied the relationships between the atomic structure, electronic property and ORR activity of Pt₃M nanoparticles including Pt₃Mn by the modeling approach and experimental [29]. These work demonstrated that Mn could enhance the activity of Pt for ORR in acid solution.

On the other hand, various manganese oxides (MnO_x), including MnO₂, MnO, Mn₂O₃, Mn₃O₄, Mn₅O₈, MnOOH, and amorphous MnO_x have been studied as ORR catalysts in alkaline solutions, due to their low cost and minimum environmental impact [30–33]. However, pristine MnO_x usually exhibits limited ORR activity due to its low electrical conductivity. Nevertheless, loading of MnO_x on conducting carbon carriers significantly improves the electrical conductivity and ORR activity, and a carbon-supported, nano-sized, manganese oxide, synthesized via a chemical depositional method, has been reported to produce relatively high ORR activity in alkaline KOH solutions [34]. Since nitrogen-doped carbon shows some metal-like behavior, we envisioned that the ORR activity of MnO_x could be further enhanced by depositing it on nitrogen-doped carbon to exploit a synergetic coupling between the two materials.

In this study, a facile, environmental friendly method has been developed to produce manganese-modified, nitrogen-doped, carbon (Mn-CN_x) by first carbonizing glycine followed by further heat-treatment with manganese salts under N₂ atmosphere. Glycine is a naturally abundant material with high nitrogen content, and thus a promising source material for preparing nitrogen-doped carbon. The resultant morphology and electrocatalytic properties of the above synthesized materials are reported here with results showing that the Mn-CN_x catalyst has similar electrocatalytic ORR activity to commercial Pt/C and has high methanol tolerance.

2. Experimental

2.1. Preparation of manganese modified nitrogen-doped carbon

Manganese modified nitrogen-doped carbon was prepared by two-step heat treatment process. An aqueous solution (50 mL) containing glycine (2.0 g) and potassium chloride (KCl, 2.0 g) was stirred for 0.5 h, and then the water was removed from the solution by heating at 353 K. The obtained mixture was carbonized at 1073 K under N₂ atmosphere for 2 h. The resultant product was ground with a ball mill, and then washed with ultrapure water until no chlorine ions were detected. The nitrogen-doped carbon made from glycine was recovered by drying at 333 K for 6 h in an oven. Potassium permanganate (KMnO₄) (300 mg) was then dissolved in 20 mL ultrapure water to which the prepared nitrogen-doped carbon (500 mg) was then added and sonicated for 20 min. The solution was dried in a vacuum oven at 333 K and the obtained powder was ball-milled and finally heat-treated at 1073 K under N₂ atmosphere for 2 h. For comparison, manganese modified Vulcan XC-72 carbon (Mn-C) and undoped-Mn carbon derived glycine (CN_x) was prepared using similar procedure to that described above.

2.2. Characterization

The Mn-CN_x was characterized by recording their X-ray diffraction (XRD) patterns on a Shimadzu XD-3A (Japan), using filtered Cu-K α radiation (40 kV, 30 mA). X-ray photoelectron spectra (XPS) was obtained using a VG Escalab210 spectrometer fitted with Mg 300 W X-ray source, and accurate binding energies

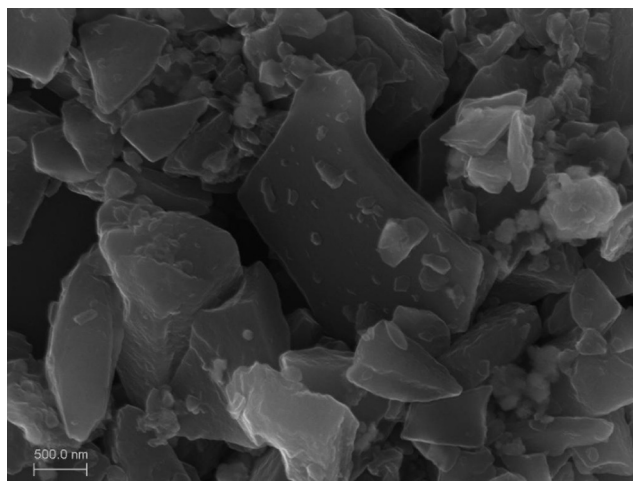


Fig. 1. SEM of Mn-CN_x.

were determined by referencing to the C 1s peak at 284.8 eV. Scanning electron microscopy (SEM) images were carried out on a Carl Zeiss Ultra Plus microscope. Raman spectra were obtained on a Ft-Raman spectroscopy (RFS 100, BRU-KER) employing Nd: YAG laser wavelength of 1064 nm.

The electrochemical measurements for ORR were carried out on a CHI650D electrochemical work station at 303 K using a three-electrode system with 0.1 M KOH as an electrolyte. For cyclic voltammetric (CV) measurements, a 5 mm diameter glassy carbon disk working electrode was used. Linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV s⁻¹ with a rotating glassy carbon disk electrode (RDE, 5 mm in diameter) as the working electrode, and the rotation rate of the disk was varied between 400 and 2500 rpm. To prepare the working electrode, 5.0 mg of catalyst was dispersed ultrasonically in 1 mL of diluted Nafion alcohol solution (0.25% Nafion) for 10 min, and 8 μ L of the suspension was pipetted onto a glassy carbon substrate. Pt wire was used as the counter electrode. The reference electrode was an Ag/AgCl (3 M KCl) electrode in the same electrolyte as the electrochemical cell. Unless otherwise specified, the loading of the catalysts in all electrochemical test in this work is ca. 0.204 mg cm⁻². Prior to measurement, O₂ was bubbled directly into the cell for at least 15 min to saturate the solution. During each measurement, O₂ was flushed over the cell solution.

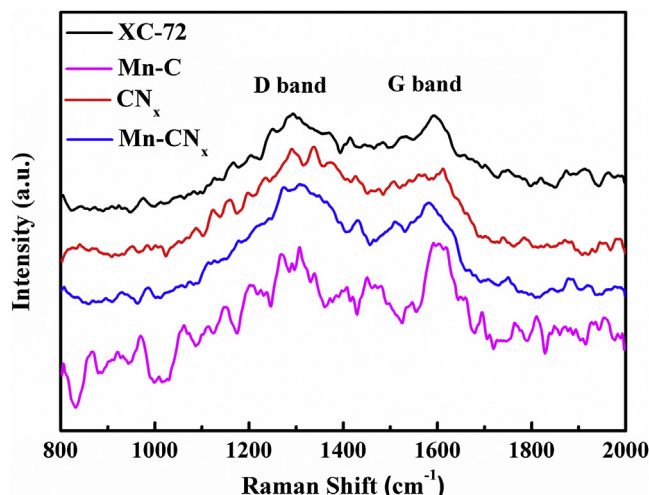


Fig. 2. Raman spectra of Mn-CN_x, CN_x, Mn-C, and XC-72.

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