



Enhanced stability of Pt electrocatalysts by nitrogen doping in CNTs for PEM fuel cells

Yougui Chen^a, Jiajun Wang^a, Hao Liu^a, Ruyin Li^a, Xuiliang Sun^{a,*}, Siyu Ye^b, Shanna Knights^b

^a Department of Mechanical and Materials Engineering, The University of Western Ontario, 1151 Richmond Street N., London, Ontario, Canada N6A 5B9

^b Ballard Power Systems Inc., 9000 Glenlyon Parkway, Burnaby, BC, Canada V5J 5J8

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ABSTRACT

Electrochemical stabilities of Pt deposited on carbon nanotubes (CNTs) and nitrogen-doped carbon nanotubes (CN_x) of different nitrogen contents are compared with accelerated durability tests (ADT) for the first time. Transmission electron microscopy (TEM) images reveal the different structures of CNTs and CN_x, and the decrease of Pt particle size with the nitrogen incorporation into CNTs. Based on the loss of electrochemical surface area (ESA) and TEM images, Pt/CN_x exhibited much higher stability than Pt/CNTs, and the Pt stability increases with the increase of nitrogen contents in the CN_x supports.

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1. Introduction

Despite the significant advances of proton-exchange membrane fuel cells (PEMFC) over the past decades, the low stability is still one of the key challenges to widespread commercialization [1,2]. The degradation of electrocatalysts (Pt or Pt alloys) and their supports is recognized as one of the main contributors to the long-term degradation of fuel cell performance.

On the conventional carbon black supports, Pt nanoparticles agglomerate into larger particles and dissolve into electrolyte because of the weak adhesion [2] and carbon black corrosion under PEMFC conditions [3]. With Pt, the corrosion of carbon black is even accelerated [4]. Thus, considerable efforts are being devoted to the development of new support materials to improve the stability of catalysts.

With a much higher graphitization degree, CNTs exhibit higher electrochemical corrosion resistance than carbon black [5,6]. Furthermore, Pt/CNTs also shows a higher stability than Pt/C [6,7]. With nitrogen atoms integrated into the graphitic structure, our group [8] and other groups [9,10] have shown that CN_x have advantages over CNTs in Pt deposition and catalytic activity. Moreover, first-principles calculations indicate a stronger adsorption of Pt on CN_x than CNTs [11,12]. Therefore, higher Pt stability can be

expected on CN_x. To our best knowledge, however, experimental studies of the stability of Pt/CN_x are still unavailable. For the first time, we demonstrate here that the electrochemical stability of Pt/CNTs can be remarkably enhanced with the nitrogen doping into the CNT matrix. Further, the Pt stability increases with the increase of nitrogen contents in the CN_x supports.

2. Experiments

CNTs and CN_x with different nitrogen amounts were synthesized via the floating catalyst chemical vapor deposition (FCCVD) method as described elsewhere [13]. Briefly, carbon paper sputtered with 30 nm Al was applied as the substrate. Ethylene, ferrocene and melamine were used as carbon, catalyst and nitrogen precursors separately. The furnace was kept at 850 °C for 5 min with a gas flow of Ar and C₂H₄ for the growth of CNTs. To synthesize CN_x, the temperature was then raised to 950 °C and kept for 5 min to dope nitrogen atoms from melamine decomposition. CN_x with different nitrogen contents were obtained with different amounts of melamine (200, 800 and 2000 mg) applied in the experiments.

Pt nanoparticles were deposited on the obtained CNTs (or CN_x) with ethylene glycol reduction method [14]. Ethylene glycol (100 ml) containing H₂PtCl₆·6H₂O and CNTs (or CN_x) at a Pt loading of 30 wt.% was refluxed at 160 °C for 3 h, and then cooled down to room temperature. The suspension was filtered and dried in a vacuum oven at 60 °C over night. Reacted with sodium borohydride,

* Corresponding author. Tel.: +1 519 661 2111x87759; fax: +1 519 661 3020.
E-mail address: xsun@eng.uwo.ca (X. Sun).

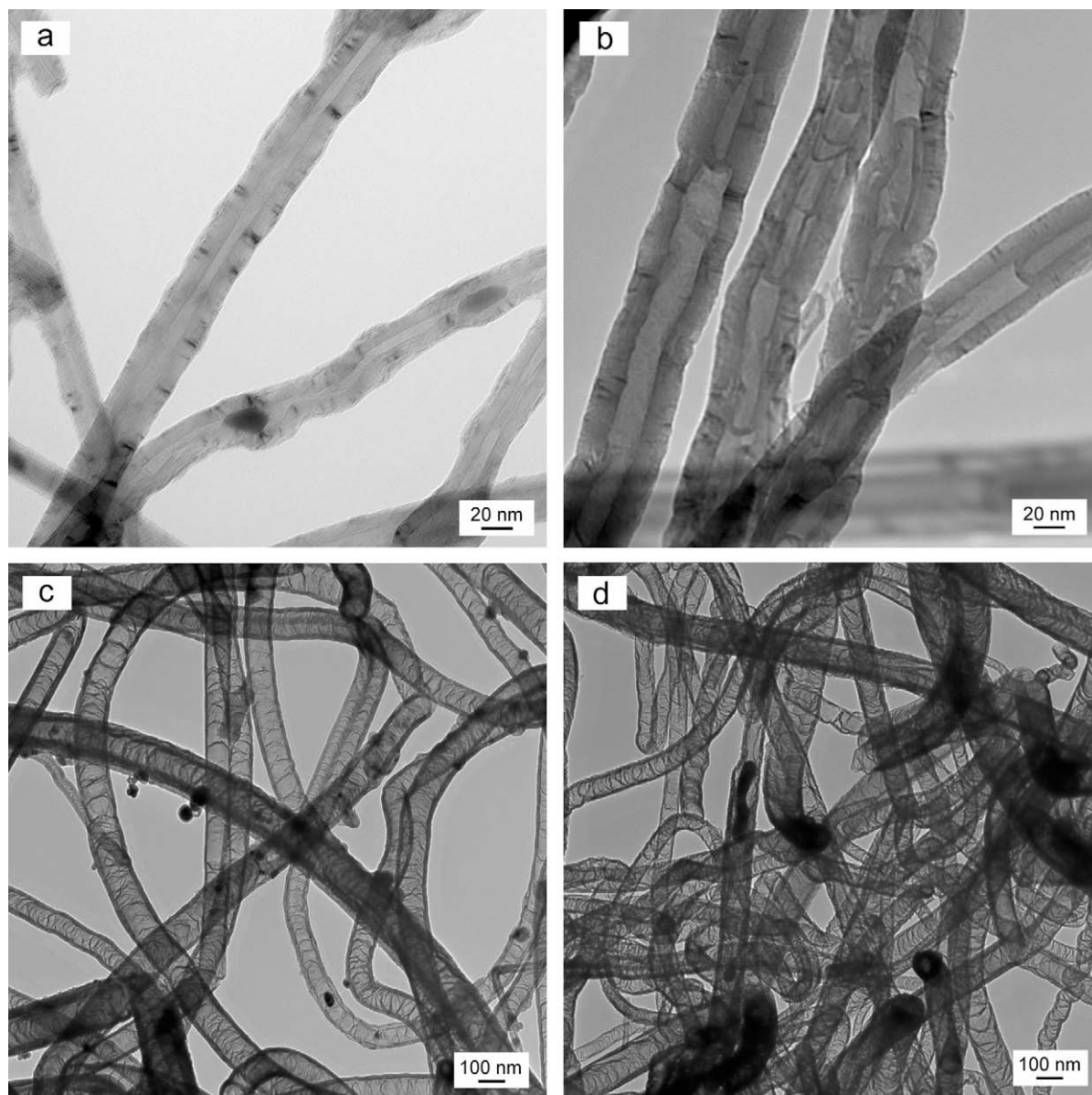


Fig. 1. TEM images of: (a) CNTs, (b) CN_x (1.5 at.% N), (c) CN_x (5.4 at.% N), and (d) CN_x (8.4 at.% N).

no changes happened to the colorless and transparent filtrate. This indicates that all H_2PtCl_6 was reduced and deposited on CNTs (or CN_x).

The ADT [15] was conducted in a conventional three-electrode glass cell with Pt wire and Ag/AgCl (3 M NaCl) serving as the counter and reference electrode separately. For convenience, all potentials are referred to standard hydrogen electrode (SHE) hereinafter. A glassy carbon electrode casted with a thin film of the same amount catalysts was applied as the working electrode. The electrode was cycled between 0.6 and 1.2 V for 4000 cycles in O_2 saturated 0.5 M H_2SO_4 . Meanwhile, full-scale voltammogram between 0.05 and 1.2 V in N_2 saturated 0.5 M H_2SO_4 were recorded periodically to track the degradation of Pt catalysts. To be compared, durability of Pt/C prepared with the same method was also tested. The scan rate was kept at 50 mV/s constantly. All the experiments were carried out at 25 °C.

TEM (JEOL 2010) was applied to characterize the structures of CNTs and CN_x , the dispersions of Pt nanoparticles on CNTs (or CN_x) before and after ADT.

3. Results and discussion

Fig. 1 shows the TEM images of CNTs and CN_x with different nitrogen amounts. Different from the hollow tube structure of CNTs (Fig. 1a), CN_x (Fig. 1b–d) exhibit a bamboo-like structure with interlinks along the tube with larger diameters. The special structure indicates that nitrogen atoms are successfully incorporated into CNT matrix, which is confirmed by X-ray photoelectron spectroscopy elsewhere [13]. Corresponding to the amounts of melamine applied in the experiments of 200, 800 and 2000 mg, the nitrogen concentration in CN_x is 1.5 (Fig. 1b), 5.4 (Fig. 1c) and 8.4 at.% (Fig. 1d), respectively [13].

Fig. 2 depicts the TEM images of Pt nanoparticles dispersed on the four supports and the corresponding particle size distribution histograms. The histograms of Pt particle size distribution are obtained on measurements of over 200 particles. The sizes of Pt/CNTs (Fig. 2a) range from 3 to 9 nm with a mean size [7] of 6.2 ± 3.4 nm. In the cases of CN_x with a nitrogen concentration of 1.5, 5.4, and 8.4 at.%, Pt nanoparticles exhibit the mean sizes of 5.0 ± 2.3

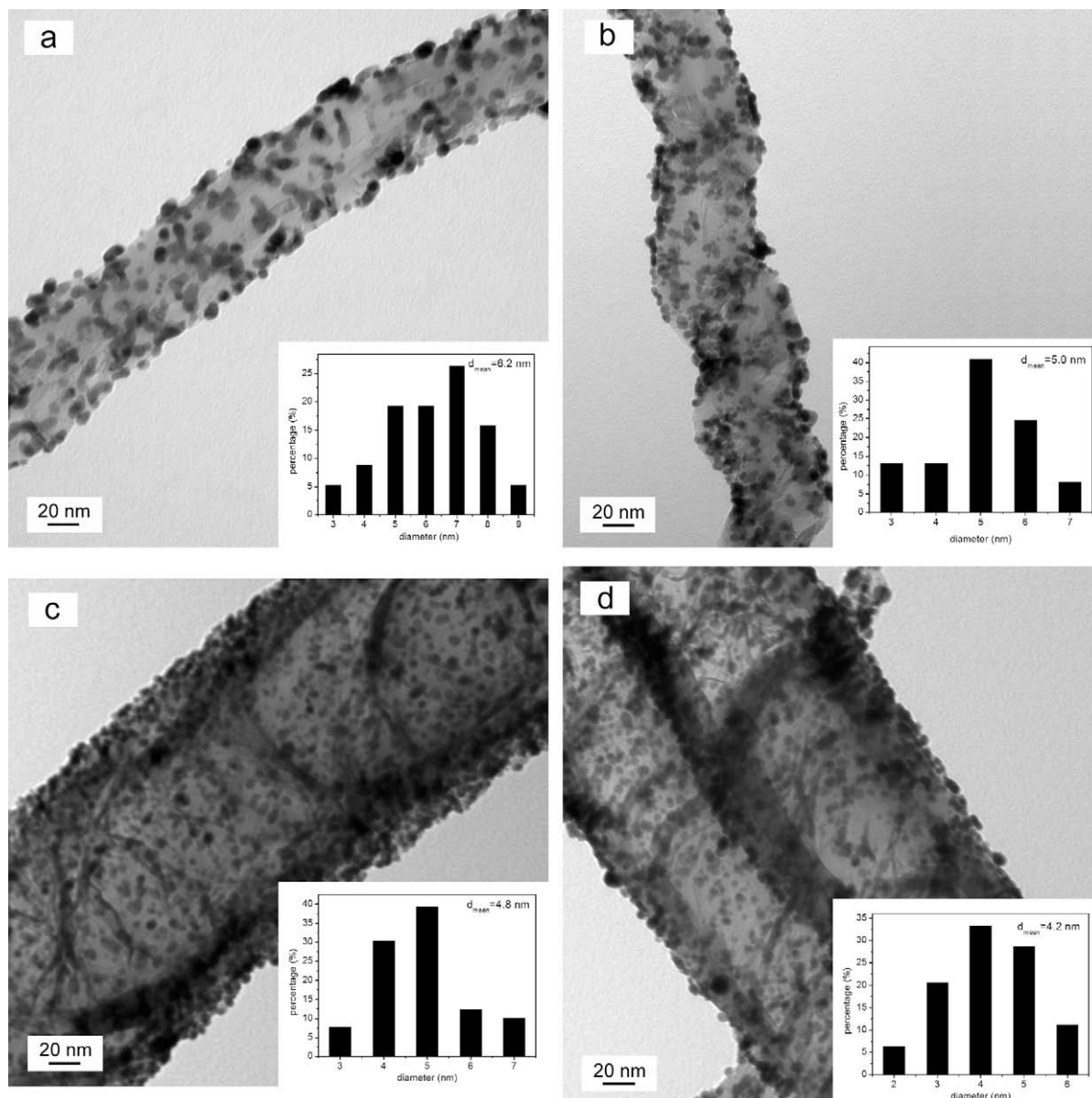


Fig. 2. TEM images and size distribution histograms (insets) of original Pt nanoparticles deposited on: (a) CNTs, (b) CN_x (1.5 at.% N), (c) CN_x (5.4 at.% N) and (d) CN_x (8.4 at.% N).

(Fig. 2b), 4.8 ± 2.0 (Fig. 2c), and 4.2 ± 1.7 nm (Fig. 2d), respectively. This indicates that smaller Pt nanoparticles with narrower distribution can be obtained on CN_x . This observation is consistent with the previous literature [8]. Furthermore, the sizes of Pt nanoparticles decrease with the increase of nitrogen contents. The better dispersion of Pt nanoparticles on CN_x can be ascribed to higher wettability, more surface structural defects and active surface by nitrogen doping [16].

ESA [7] is one critical parameter for characterizing a PEMFC catalyst. A larger ESA means more active sites for catalysis. The performance degradation of PEMFCs is largely due to the loss of ESA [1,2]. During voltammetric cycling between 0.6 and 1.2 V in O_2 saturated sulfuric acid, which mimics the cathode of PEMFCs, the oxidation and reduction of Pt accelerate its dissolution and agglomeration. Fig. 3a–e represents the changes of voltammograms during ADT at different intervals. Normalized with the initial one, the degradations of the ESA are plotted in

Fig. 3f. Similar to previous studies [6,7], the durability of Pt/C is much lower than that of Pt/CNTs in this work. After 4000 cycles, only 4.6% of the initial ESA of Pt/C is remained while 11.2% of the initial ESA for Pt/CNTs. It is also evident that Pt/ CN_x have a higher stability than Pt/CNTs. Pt/ CN_x (1.5 at.% N), Pt/ CN_x (5.4 at.% N) and Pt/ CN_x (8.4 at.% N) retains 20.2%, 26.6% and 42.5%, respectively after 4000 cycles. Compared with Pt/CNTs, Pt/ CN_x with smaller particle sizes exhibits higher electrochemical stability. Furthermore, the stability increases with the nitrogen contents.

The degradation of ESA is caused by the dissolution and agglomeration of the Pt nanoparticles [1,2]. To investigate the changes of Pt nanoparticles, the TEM images and the associated particle size distribution histograms after ADT are presented in Fig. 4. Notable agglomerations occur to all the four Pt electrocatalysts, resulting in much larger particles and wider distribution. After 4000 voltammetric cycles, Pt/CNTs reveal a broad dispersion

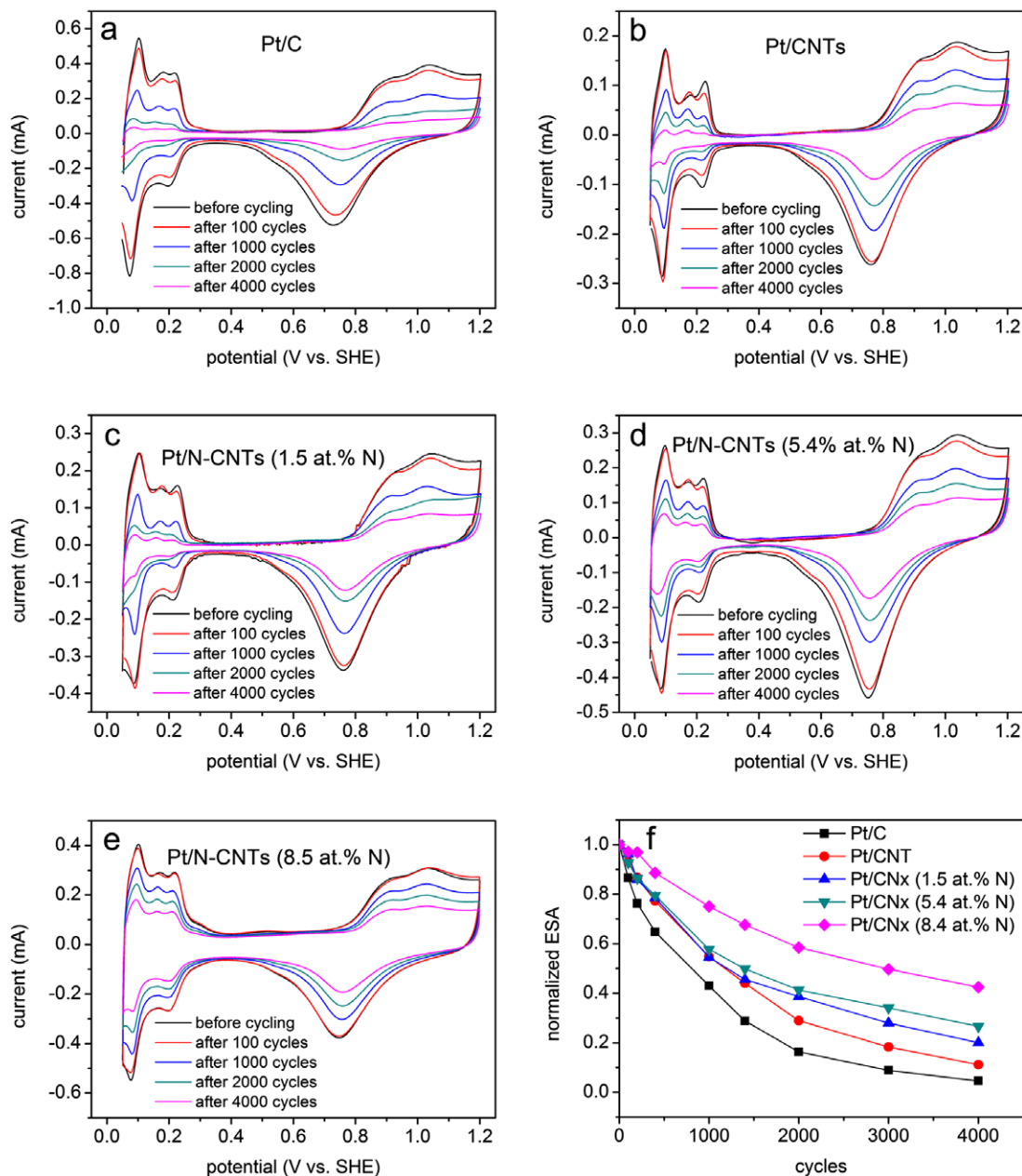


Fig. 3. Cyclic voltammograms of: (a) Pt/C, (b) Pt/CNTs, (c) Pt/N-CNTs (1.5 at.% N), (d) Pt/N-CNTs (5.4 at.% N), (e) Pt/N-CNTs (8.4 at.% N), and (f) the comparison of the degradations of the five catalysts. Scan rate: 50 mV/s.

with a mean size of 13.6 ± 6.1 nm (Fig. 4a), much larger than 6.2 ± 3.4 nm before ADT (Fig. 2a). Dissolution and aggregation also occur to Pt nanoparticles on CN_x (Fig. 4b–d), but to a lesser extent. The mean size of Pt/ CN_x after ADT is 11.0 ± 5.4 , 8.7 ± 4.9 and 7.4 ± 4.1 nm, respectively for the nitrogen contents of 1.5, 5.4 and 8.4 at.%.

ADT and TEM results indicate that the presence of nitrogen in CNTs helps the stabilization of Pt catalysts, which is critical for the long-term performance of PEMFC. This can be explained as follows. Firstly, the nitrogen atom has one more electron than the carbon atom. Substituted by nitrogen, the interaction between Pt nanoparticles and the delocalized π bond [17] is enhanced. Moreover, similar with the protection of Pt nanoparticles by other protective agents with electron-rich functional groups, Pt nanoparticles can be stabilized by the lone electron pair in nitrogen

atoms. Additionally, the higher stability of Pt/ CN_x can be credited to the stronger binding between Pt atoms and the CN_x supports, which has been confirmed with first-principles studies [11,12]. The improved adsorption results from activation of the nitrogen-neighboring carbon atoms due to the large electron affinity of nitrogen [11]. With the doping of nitrogen atoms, there is an increment of up to 1.35 eV for the binding energy between Pt atom and CNT [12].

4. Conclusions

CNTs and a series of CN_x with different nitrogen amounts (1.5, 5.4 and 8.4 at.%) have been synthesized with the FCCVD method. The structure and tube diameter are altered with nitrogen

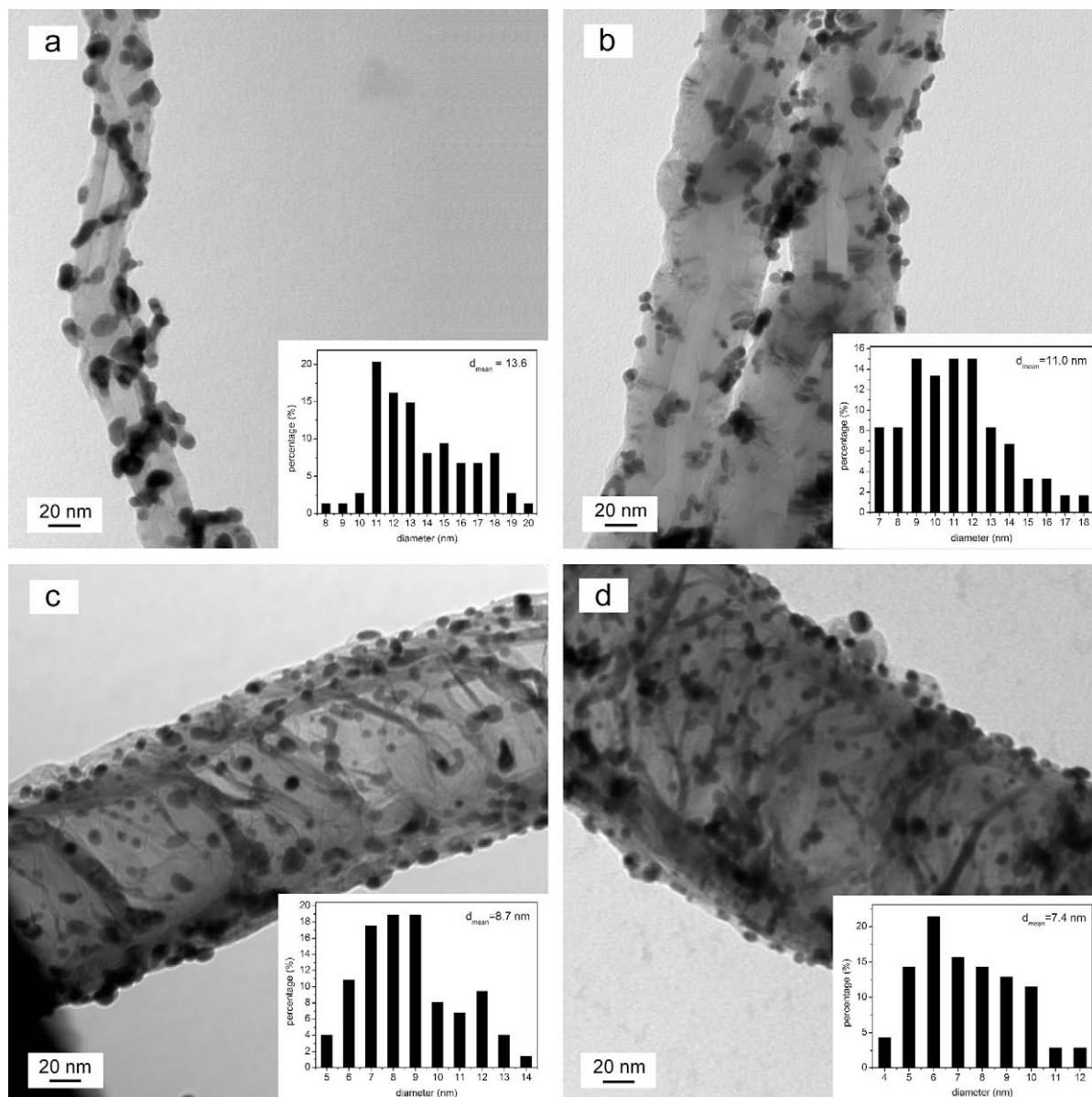


Fig. 4. TEM images and size distribution histograms (insets) of Pt electrocatalysts after ADT. (a) Pt/CNTs; (b) Pt/N-CNTs (1.5 at.% N); (c) Pt/N-CNTs (5.4 at.% N); (d) Pt/N-CNTs (8.4 at.% N).

doping. The sizes of Pt nanoparticles on the four supports decrease with the increase of nitrogen contents. With the doping of nitrogen into CNT supports, not only the ESA increases, the stabilities of the Pt catalysts are also remarkably enhanced, and the ESA and stability is further increased with higher nitrogen amounts. Among the five catalysts, Pt/C has the lowest stability. Only 4.6% of the initial ESA is remained after 4000 voltammetric cycles. Pt/CN_x with the highest amount of nitrogen (8.4 at.%) results in the highest stability. 42.5% of the initial ESA is retained after 4000 voltammetric cycles. This work is of great importance for seeking PEMFC catalysts with high performance and durability.

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