Polydopamine-derived, *in Situ* N-doped 3D Mesoporous Carbons for Highly Efficient Oxygen Reduction

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ABSTRACT

N-doped carbon materials have been triggered huge interest as the alternative electrocatalysts to replace noble metals. The intrinsic unit activity of N-doped carbons cannot yet match that of metals, but by maximizing carbon's extrinsic surface areas to increase the number of active sites, the apparent performance of N-doped carbons can be substantially promoted. Herein, polydopamine was first employed to derive N-doped mesoporous carbons (NMCs) by a facile hard-templating method. The newly developed NMC-900 displays highly catalytic efficiency towards oxygen reduction reaction (ORR) comparable to that of Pt/C and superb stability greatly surpassing Pt/C, which can be attributed to its fascinating componential and structural features. The componentially favorable graphitic N and pyridinic N afford highly efficient and stable metal-free active sites towards the ORR. The structurally large surface areas (536 m²/g) together with well-aligned 3D mesoporous architecture provide the sufficiently exposed active sites and unimpeded reaction channels for the ORR. Our finding would advance knowledge for the rational design of future high-performance carbon electrocatalysts.

Keywords: Mesoporous carbons, Polydopamine, N-doping, Oxygen reduction, Metal-free

1. Introduction

Over the past decades, electrochemically renewable energy conversion and storage have been keenly pursued to meet the challenge of global warming and dwindling fossil fuels [1-3]. However, the scarce and nondurable noble-metal electrocatalysts were popularly used, such as Pt in the oxygen reduction reaction (ORR) [4-8] and hydrogen evolution reaction (HER) [9-11] and Ru and Ir in the oxygen evolution reaction (OER) [12-14]. To search superior alternatives to replace these noble-metals, two key factors that govern catalytic activities have to be considered simultaneously: the intrinsic unit activity of active sites and the number of exposed active sites (specific surface areas) [15, 16].

At first, large amount of electrocatalysts with metal species as the active sites have been developed for electrochemical reactions [17-20]. However, in practical implementation, one significant drawback associated with metal-based catalysts is easily and unavoidably deactivated caused by different degradation mechanisms during long-term catalytic process, such as fouling, chemical poisoning, sintering and leaching [21-23]. On the other hand, the metal-free N-doped carbon materials have sprung up rapidly in last few years, due to the low cost, and particularly high stability of carbon active sites without similar deactivation and fuel crossover problems [4]. The intrinsic unit activity of N-doped carbons cannot yet match that of metal benchmarks, but by optimizing the extrinsic surface areas to increase the number of active sites, the apparent performance of N-doped carbons can be promoted to the levels that is comparable to or even outperform that of metal-based catalysts [16].

So far, N-doped carbons have been significantly developed, especially based on the 2D graphene or 1D carbon nanotubes, but the poor tunability of surface areas limited their performance to the levels of metal counterparts [24-26]. 3D N-doped mesoporous carbons

(NMCs) seem to be an ideal choice owing to their extraordinarily high surface areas and 3D pore microstructures [27, 28]. Currently, some N-containing precursors, such as aniline [29], pyrrole [30], and o-phenylenediamine [15], have been employed for doped mesoporous carbons using the straightforward hard-templating approach. However, the certain polymerization catalysts are necessary in harsh reaction conditions. Dopamine (DA) can self-polymerize under alkaline condition to produce a continuous film of polydopamine (PDA), which can deposit on the surface of any substrate [31, 32]. Compared with aforesaid precursors, DA is nontoxic and the polymerization reaction can proceed in a mild condition in lieu of extra catalysts. Recently, we have reported that PDA/graphene and PDA/carbon nanotube nanocomposites can be applied to derive single- and dual-doped carbons as novel highly efficient electrocatalysts for ORR, OER and HER [26, 33-35]. However, PDA has never been explored for the fabrication of NMCs.

As a continuous study, we herein first report the facile synthesis of PDA-derived 3D NMCs using the hard-templating method. The resulting metal-free NMCs have remarkable componential and structural features, including *in situ* formed favorable N species, large surface areas and well-aligned mesoporous structures, which render the NMCs as more favorite candidates in their electrochemical applications as evident from their superior ORR performance comparing to commercial Pt/C.

2. Experimental

2.1. Materials preparation

2.1.1 Preparation of PDA/SBA-15 hybrids.

In a typical experiment, 200 mg SBA-15 was mixed with 400 mg DA dissolved in 180 mL DI water. The mixture was sonicated for 10 min, 20 mL PBS buffer (0.4 M, pH = 8.5) was added, and the mixture was then stirred for 24 h at room temperature. The container was covered with aluminum foil with several small holes. The PDA/SBA-15 hybrids were obtained by centrifugation and washing with water for three times.

2.1.2 Carbonization of PDA/SBA-15 hybrids.

The as-prepared hybrids were carbonized in a temperature-programmable tube furnace under N₂ atmosphere at 400 °C for 2 h with a heating rate of 1 °C min⁻¹, which was followed by further heat treatment at 900 °C (800 or 1000 °C) for 3 h with a heating rate of 5 °C min⁻¹.

2.1.3 Synthesis of N-doped mesoporous carbons (NMCs).

The silica templates were etched out by 2.0 M NaOH at 80 °C for 24 h to obtain the NMCs, and this procedure was repeated three times for removing silica template completely. The collected powder was washed with water for several times and dried under vacuum at 80 °C.

2.2 Materials characterization

Fourier transform infrared (FTIR) spectra were collected on the transmission module of a Thermo Nicolet 6700 FTIR spectrometer at 2 cm⁻¹ resolution and 64 scans. TEM (transmission electron microscopy) images were acquired on a Talos F200X G2 microscopy. TEM elemental mapping was obtained through the EDAX detector attached to the Talos F200X G2. The Raman spectra were collected on the iHR550 from HORIBA Scientific equipped with a 532 nm solid laser as the excitation source. X-ray diffraction (XRD) was

performed on the Miniflx-600 (Rigaku Ltd.) under ambient condition using a Cu K α X-ray. XPS analysis was conducted on Axis Ultra spectrometer (Kratos Analytical Ltd.) with monochromated Al K α radiation at ca. 5×10^{-9} Pa. Nitrogen adsorption-desorption isotherm was collected on the Tristar II (Micrometrics) at 77 K. Pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) model using the adsorption branch on isotherm. The specific surface areas of the materials were calculated using the adsorption data at a pressure range of $P/P_0 = 0.05 - 0.3$ by the Brunauer-Emmett-Teller (BET) model.

2.3 Electrochemical measurements

For the electrochemical tests, 2 mg of the catalyst was dispersed in 1 ml DI water. The mixture was slightly ultra-sonicated to obtain a homogenous catalyst ink. To prepare the working electrode for electrochemical measurements, 20 μ l of the ink was dipped on a mirror polished glass carbon electrode. 5 μ l of 0.5 wt. % Nafion aqueous solution was then dropped on the electrode and dried at room temperature. After that, the working electrode was inserted into a three-electrode cell setup, which is composed of a platinum counter electrode, an Ag/AgCl/KCl (4 M) reference electrode in a glass cell containing 100 ml 0.1 M KOH aqueous electrolyte. A flow of O₂ was maintained over the electrolyte solution (0.1 M KOH) during recording electrochemical data in order to ensure its continued O₂ saturation. Cyclic voltammogram (CV), linear sweep voltammogram (LSV), and rotating disk electrode (RDE) tests were carried out using a glassy carbon rotating disk electrode. The scan rate of CVs was kept at 50 mVs⁻¹ while that for the LSVs and RDE tests was set to 5 mV s⁻¹. The data were recorded using an electrochemical analysis workstation (CHI 760C, CH Instruments, USA).

The Koutecky-Levich plots were obtained by linear fitting of the reciprocal rotating speed versus reciprocal current density collected at different potentials from -0.4 to -0.8 V. The overall

electron transfer numbers per oxygen molecule involved in a typical ORR process were calculated from the slopes of the Koutecky-Levich plots using the following equation:

$$1/j_D = 1/j_k + 1/B\omega^{1/2} \quad (1)$$

where j_k is the kinetic current in amperes at a constant potential, ω is the electrode rotating speed in rpm, and B is the reciprocal of the slope, which was determined from the slope of Koutecky-Levich plots based on the Levich equation as followed:

$$B = 0.2 n F A \nu^{-1/6} C_{O_2} D_{O_2}^{2/3} \quad (2)$$

where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96,485 C mol⁻¹), D_{O_2} is the diffusion coefficient of O₂ in 0.1 M KOH (1.9×10⁻⁵ cm s⁻¹), ν is the kinetic viscosity, and C_{O_2} is the concentration of O₂ (1.2×10⁻³ mol L⁻¹). The constant 0.2 is adopted when the rotating speed is in rpm.

Rotating ring-disk electrode (RRDE) voltammogram measurements were conducted on an RRDE configuration (Pine Research Instrumentation, USA) with a 320 μm gap Pt ring electrode. The linear sweep voltammograms were recorded in O₂ saturated 0.1 M KOH at 1600 rpm. The disk was set to scan at 5 mV s⁻¹ from 0.2 to -0.8 V and the ring was set at 0.5 V. The collecting efficiency of the RRDE (N) was 0.37. The peroxide yield (HO₂⁻%) and the electron transfer number (n) were calculated as follows:

$$HO_2^-\% = 200 \times I_r / N / (I_d + I_r / N) \quad (3)$$

$$n = 4 \times I_d / (I_d + I_r / N) \quad (4)$$

where I_d is the disk current and I_r is the ring current.

The stability and resistance to methanol crossover effect were tested in the same setup as that for the RDE test in O₂ saturated 0.1 M KOH aqueous electrolyte and were performed at a static potential of -0.5 V and -0.2 V, respectively, for the chronoamperometry at room temperature.

Scheme 1. Fabrication of PDA-derived NMC-900. SBA-15 was first mixed with DA in PBS buffer to obtain PDA/SBA-15 hybrids. After the pyrolysis at 900 °C and etching in 2M NaOH, NMC-900 was facilely obtained.

3. Results and Discussion

As shown in Scheme 1, self-polymerization of DA within the pores of SBA-15 was carried out in PBS buffer (pH~8.5) to obtain PDA/SBA-15 hybrids, which were then pyrolyzed and etched to derive the NMCs. Different pyrolysis temperature of 800, 900 and 1000 °C were employed, but

the NMCs were only achieved at 800 and 900 °C, the corresponding NMCs were designated as NMC-800 and NMC-900, respectively.

The microstructures of the NMCs were examined by TEM. The well-defined linear array of mesoporous structures is observed for both NMC-800 and NMC-900, well inheriting the geometric morphology of the original SBA-15 templates (Figures 1A, 1B, and S1-S3) [5]. The enlarged view of the TEM image (Figure 1C) shows highly-organized mesopores of ~ 4 nm and continuous thin walls with the thickness of ~ 5 nm, which can be further confirmed clearly through high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 1D). Apparently, the formation of thin walls benefits from the unique capability of PDA, *i.e.*, PDA can create continuous thin films easily. Typical elemental mapping images of NMC-900 (Figures 1E-1H) illustrate the homogeneous distribution of N and O elements, also reinforcing the uniform deposition of PDA on SBA-15. The textural properties of the NMCs were evaluated by N₂ adsorption-desorption isotherms. Both NMC-800 and NMC-900 exhibit type-IV isotherm characteristics with distinct hysteresis loops for mesoporous materials (Figure 1E). The Barrett-Emmett-Teller (BET) surface areas are 387 m²/g for NMC-800 and 536 m²/g for NMC-900 with their mesopore sizes centered at 3.5 and 4.5 nm, respectively, according to the Barrett-Joyer-Halenda (BJH) model. Raman spectra (Figure S4) show the NMC-900 has a lower I_D/I_G ratio (0.97) than that of the NMC-800 (1.07), indicating its higher graphitization degree and better electrical conductivity. Obviously, the higher pyrolysis temperature is conducive to a better mesoporous carbon structure (higher surface areas and better graphitization). Accordingly, 1000 °C was employed to pyrolyze PDA/SBA-15, but

no porous structure was observed. That might be caused by the fact that more carbon are burnt off at a higher temperature and thus leads to structural collapse of mesopores.

Figure 1. (A) TEM image of NMC-900. (B) The enlarged TEM image from the red rectangular area in (A). (C) The high magnified TEM and (D) HAADF-STEM images of NMC-900. (E-H) HAADF-STEM image of NMC-900 and elemental mapping images of C, N and O, respectively.

(I) The nitrogen adsorption-desorption isotherms, and (J) the pore size distribution curves of NMC-800 and NMC-900.

The characteristic peaks of SBA-PDA at 1502 and 1615 cm^{-1} in the FTIR spectra (Figure 2A) coincide with the indole or indoline structure of PDA, indicating the successful deposition of PDA [26, 33, 34]. The chemical status of these elements was accurately evaluated by the X-ray photoelectron spectroscopy (XPS) as shown in Figures 2 and S6. XPS survey scan indicates the presence of carbon, nitrogen (3.0 %) and oxygen (9.1 %) in NMC-900 (Figure 2B). Additionally, the high-resolution N 1s spectra can be deconvoluted into three peaks centered at 398.1, 400.7 and 402.9 eV, which can be assigned to pyridinic N (0.9 %), graphitic N (1.8 %) and oxidized N (0.3 %), respectively (Figure 2C) [36, 37]. The high-resolution O 1s peaks are mainly deconvoluted into three peaks associated with C=O (532.7 eV, 5.2 %), HO-C=O (530.5 eV, 3.0 %) and C-OH (534.5 eV, 0.9 %) (Figure 2D), and the introduction of large amount of O species from PDA improves the surface hydrophilicity of resulting electrocatalysts and further facilitates their catalytic reactions.

Figure 2. (A) FTIR spectra of SBA-15 and SBA-PDA. (B) XPS scan of C, N and O. (C) XPS spectra: N 1s, O 1s, and survey of NMC-900.

To evaluate the catalytic activity of these nanostructured metal-free NMCs, ORR was employed as a model reaction, which is a cornerstone reaction that typically operates in fuel cells, metal-air batteries and chlor-alkali electrolyzers [38]. Cyclic voltammetry (CV) was conducted in both O_2 and N_2 saturated electrolytes (Figures 3a and S7). As shown in Figure 3a, when the electrolyte was saturated with N_2 , a quasi-rectangular

voltammogram without obvious redox peak is obtained for NMC-900 due to the typical supercapacitance effect on porous carbon materials [6], and while one well-defined characteristic ORR peak, centered at -0.18 V with a reaction current of -2.8 mA cm⁻², can be observed in O₂-saturated solution. Compared with NMC-800, the peak potential for NMC-900 is more positive than that of NMC-800 (-2.3 V), and the ORR reaction current on NMC-900 is apparently higher than that on NMC-800 (-2.2 mA cm⁻²), suggesting a more facile ORR process on the NMC-900.

A series of linear sweep voltammograms (LSVs) were collected on a rotating disk electrode (RDE) at 1600 rpm (Figure. 3B), which further revealed the lower onset potential and higher ORR current density on NMC-900 than NMC-800 electrodes, consistent with the abovementioned CVs results. Noteworthy is that the onset potential on NMC-900 is nearly identical to that on commercial Pt/C catalyst. At -0.6 V, NMC-900 shows an ORR current density of -5.2 mA cm⁻², higher than that of NMC-800 (-3.9 mA cm⁻²) and Pt/C (-4.6 mA cm⁻²), indicating outstanding ORR activity on NMC-900. Impressively, the diffusion-limited current plateau of Pt/C at -0.4~-0.8 V was not observed on both NMC-800 and NMC-900, principally attributed to the large surface area and 3D mesoporous structures of the NMCs, which can provide abundantly exposed active sites and unimpeded diffusion channels for the ORR process. To further prove that, the ORR activity of 2D N-doped graphene (NG) and 3D CMK-3 were examined (Figure 3B). NG has the N-doped active sites but no mesoporous structure [25], while the case for CMK-3 is contrary [5]. Expectedly, both of them exhibit poor ORR activity compared with NMCs, indicating the large number of exposed active sites and benign porous structure are two indispensable factors for a good ORR electrocatalysts.

The rotating ring-disk electrode (RRDE) technique was further employed to quantify the ORR efficiency by monitoring the formation of intermediate peroxide species during the ORR process (Figures 4C and 4D) [39]. Remarkably, only 13-17 % H_2O_2 yields on NMC-900 over a wide potential range from -0.2 to -1.0 V, corresponding to the electron transfer number (n) from 3.7 to 3.9. On the other hand, NMC-800, its n ranges from 3.3 to 3.7, gives ~10 - 35% H_2O_2 under identical conditions. These results indicate the highly electrocatalytic efficiency of NMC-900 with a $4e^-$ dominated pathway.

Figure 3. (A) CV curves of NMC-900 in N_2 and O_2 -saturated 0.1 M KOH solution. (B) LSVs at a sweep rate of 5 mV s^{-1} of NG, CMK-3, NMC-800, NMC-900 and Pt/C. (C) RRDE voltammograms at 1600 rpm in O_2 -saturated 0.1 M KOH solution. (D) H_2O_2 yield (blue, primary

Y-axis) and the corresponding electron transfer number (red, second Y-axis) of NMC-800 and NMC-900. (E) The kinetic limiting current density (J_k) calculated at different potentials for NMC-800, NMC-900 and Pt/C (see Figure S8). (F) the corresponding difference in the current density at 0.025 V plotted against scan rate (see Figure S9), the calculated C_{dl} values of NMC-800 and NMC-900 are shown as the inset.

To more clearly confirm the potential suitability of NMCs as the ORR catalysts, the kinetic limiting current density (J_k) was obtained from the intercept of linearly fitted Koutecky-Levich (K-L) plots at different potentials from -0.4 to -0.8 V (Figures 3E and S8). Impressively, NMC-800 and NMC-900 possess nearly identical J_k value, about 14.9 and 15.0 mA cm⁻², respectively, which is much close to that of Pt/C (16.3 mA cm⁻²) at -0.6 V, suggesting the excellent ORR performance of this new family of NMCs. Additionally, the J_k values of both NMCs sharply increase to ~25 mA cm⁻² at the potential of -0.8 V, much higher than that of Pt/C (15.3 mA cm⁻²), implying the performance of NMCs can be potentially further improved. The behavior of large J_k at high potentials can be also reasonably interpreted by the structural features of NMCs as aforesaid, i.e. large surface areas and unique 3D mesoporous architecture.

The efficient activity of the NMC-900 catalyst toward ORR could be ascribed to the following aspects: (1) In particular, favored graphitic N and pyridinic N species clearly dominate in NMC-900, *in situ* transformed from the inherent pyrrolic N of PDA. Graphitic N and pyridinic N are generally considered to be responsible for ORR activity while pyrrolic N has little effect [40, 41]. Ruoff *et al* found pyridinic N can improve the onset potential by facilitating reductive O₂ adsorption and graphitic N can boost the J_k [42]. Dai *et al* claimed graphitic N at the edge of graphene could act as the most active catalytic site for ORR by reducing the OOH intermediate adsorption energy [43]. Jung *et al* reported the

inter-conversion between the graphitic and pyridinic sites can occur within a ORR catalytic cycle [44]. Consequently, the desirable N components enable our novel NMC samples to be the efficient ORR electrocatalysts. (2) The well-organized mesoporous structure and large surface areas of 3D NMCs, confirmed by nitrogen adsorption, yield a large electrochemical double-layer capacitance (C_{dl}), which is proportional to the electrochemically active surface area. As shown in Figures 3F and S9, NMC-900 owns a much higher C_{dl} (29.1 mF cm^{-2}) than that of NMC-800 (16.7 mF cm^{-2}), and this would provide sufficient active sites and smooth mass transportation, reassuring the highly-efficient ORR electrocatalytic process on NMC-900. (3) The better graphitization of NMC-900 gives rise to high electrical conductivity, and the hydrophilic surfaces arised from abundant O groups make exposed active sites readily available, both accelerating ORR kinetics.

Figure 4. (A) The current-time chronoamperometric response of NMC-900 and Pt/C in O_2 -saturated 0.1 M KOH solution. (B) The current-time chronoamperometric response of NMC-900 and Pt/C in O_2 -saturated 0.1 M KOH solution before and after addition of 3 M methanol.

Furthermore, the long-term stability of NMC-900 and commercial Pt/C was assessed through chronoamperometric measurement in O₂-saturated 0.1 M KOH. As shown in Figure 4A, NMC-900 exhibits a very slow attenuation over 20 h, retaining 97.2 % of the initial current, whereas Pt/C shows nearly 40 % loss of its initial current over the same time period, confirming the outstanding ORR stability of carbon active sites in alkaline environment. Additionally, the methanol crossover effect was also evaluated on both NMC-900 and Pt/C (Figure 4B). After adding 3M methanol to the electrolyte, the original cathodic ORR current of NMC-900 remains almost unchanged, whereas the corresponding current on Pt/C instantaneously shift from a cathodic ORR current to a reversed anodic current owing to the methanol oxidation reaction on Pt/C. The remarkable stability and excellent selectivity of NMC-900 make it highly promising as an ORR electrocatalyst in practical applications.

4. Conclusion

In conclusion, by means of robust PDA chemistry, a novel family of 3D N-doped mesoporous carbons has been fabricated via an easy hard-templating strategy. The resultant carbons possess *in situ* formed favorable N components, well-organized mesoporous structure and large surface areas, and thus exhibit an outstanding performance with superior activity and extreme durability in ORR. Considering the versatile physicochemical property of PDA, our work sheds new lights on the design of PDA-based heteroatom-doped or metal-N decorated carbon materials, which would be highly promising alternatives to noble metals in future electrocatalytic applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/xxx>.

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Supporting Information

Experimental section

Synthesis of SBA-15

In a typical synthesis, 1.6 g (0.32 mmol) of Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_w \sim 5800$) and 2.2 g (30 mmol) of potassium chloride were dissolved in 60 g of 2.0 M HCl at 38 °C for overnight. Then, 4.2 g (20 mmol) of tetraethylorthosilicate was added to the transparent solution with vigorous stirring for 8 min and the mixture was left under static condition at the same temperature for 24 h. The mixture was subsequently treated at 130 °C for another 24 h in an autoclave. The as synthesized SBA-15 was collected by filtration, washed by water twice, dried at 100 °C for overnight and finally calcined at 550 °C for 5 h in the air to get the final product.

Synthesis of CMK-3

CMK-3 mesoporous carbon was synthesized using SBA-15 as a hard template via a nanocasting method. Typically, 1.25 g (3.63 mmol) of sucrose was dissolved in 5 g of water containing 0.14 g (1.4 mmol) of H_2SO_4 . 1 g of SBA-15 powder was then dispersed in the above solution and stirred for 12 h at room temperature. The mixture was then heat treated at 100 °C for 6 h and subsequently at 160 °C for another 6 h in air. The impregnation process was repeated once with another solution containing 0.8 g (2.32 mmol) of sucrose and 5 g of water containing 0.09 g (0.9 mmol) of H_2SO_4 . The dark brown composites were completely carbonized at 900 °C for 5 h in argon at a heating rate of 2 °C /min. To remove the silica template, the as-prepared carbon-silica composites were stirred in a 10 % hydrofluoric acid for one day then washed by water and ethanol until neutral and finally dried at 100 °C for overnight.

Synthesis of N-doped graphene (NG)

NG was synthesized by annealing GO powder in 20 % NH_3/Ar at 900 °C for 5 h with a heating rate of 5 °C/min. After annealing, the furnace was cooled down to room temperature under the same atmosphere.

Figure S1. TEM images of SBA-15 with different magnification.

Figure S2. (A) TEM and (B) HAADF-STEM images of NMC-900.

Figure S3. TEM images of NMC-800.

Figure S4. Raman spectra of NMC-800 (red) and NMC-900 (blue).

Figure S5. XRD pattern of NMC-900 catalyst. Only two distinct XRD characteristic peaks are observed at 2θ around 26.1° and 43.2° , which are assigned to the (002) and (101) planes of graphitic carbon.

Figure S6. XPS high-resolution spectra of C1s of NMC-900.

Figure S7. CV curves of NMC-800 in N_2 and O_2 -saturated 0.1 M KOH solution.

Figure S8. (A, C and E) LSVs at different rotating speeds from 0 to 2400 rpm with an increment of 400 rpm between each voltammogram, (B, D and F) K-L plots obtained at different potentials: -0.4, -0.5, -0.6, -0.7 and -0.8V. (A, B): NMC-800, (C, D): NMC-900 and (E, F): Pt/C.

Figure S9. CV curves at different scan rates (2, 4, 6, 8 and 10 mV s^{-1}) of (A) NMC-800 and (B) NMC-900.