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A facile surface modification of Nafion membrane by the formation of self-polymerized dopamine nano-layer to enhance the methanol barrier property

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ABSTRACT

By immersing Nafion membrane into dopamine aqueous solution under mild conditions, a series of modified Nafion membranes for the application in direct methanol fuel cell (DMFC) were fabricated. High resolution scanning electron microscope and Fourier transform infrared spectra characterization revealed that a dense nano-layer around 50 nm was formed and adhered tightly to Nafion surface. Small-angle X-ray scattering, wide X-ray diffractometer and positron annihilation lifetime spectroscopy analysis implied that the microstructure such as phase-separated structure and ion-cluster channel of Nafion layer was slightly changed after surface modification. The influence of modification conditions including pH value, dopamine concentration and immersing time upon membrane performance was investigated. Due to the effective reduction of methanol dissolution and enhancement of methanol diffusion resistance, the methanol crossover of the modified membranes was dramatically suppressed by about 79% from 3.14×10^{-6} to about 0.65×10^{-6} cm^2 s^{-1}. Meanwhile, the proton conductivity of the modified membranes was slightly decreased to be around 0.06 S cm^{-1}. Consequently, the comprehensive performance of the modified membranes was improved by about five times. These results hinted the application promises of such modified Nafion membranes in DMFC.

1. Introduction

Perfluorosulfonic polymer such as Nafion (Dupont) is the most common membrane electrolyte used in polymer electrolyte fuel cell (PEFC) and direct methanol fuel cell (DMFC) in virtue of its excellent chemical, mechanical and thermal stability and high proton conductivity in hydrated state [1–3]. However, methanol crossover from the anode to the cathode through Nafion membrane, which drastically reduces the DMFC performance due to the mixed potential effect and catalyst poisoning, seriously retards the technological development of DMFC [4,5].

Previous studies revealed Nafion, with hydrophobic polyethylene backbone and pendant hydrophilic sulfonated side chains, displayed a phase-separated structure which provided a series of ion-cluster channels to facilitate methanol permeation across the membrane [6–8]. The methanol transport through Nafion membrane could be elucidated by solution-diffusion mechanism [9]. After dissolving into the membrane surface, methanol molecules diffuse primarily through the ion-cluster channels constructed by the hydrophilic domains [6,8]. Therefore, tremendous efforts have been devoted to suppress methanol crossover by tuning the surface and/or internal microstructure of the commercial Nafion membrane. The membranes explored can be summarized as follows: (i) cation exchanged membrane [10–12]: to reduce the size of the ion-cluster channel by replacing H^+ of sulfonic acid group with other cation (e.g. cesium ion, calcium ion and ion lipid); (ii) blend membrane [13–15]: to alter the microstructure and thus reduce the channel size for methanol diffusion by blending alcohol barrier polymer (e.g. polyaniline, polyvinylidene fluoride and polyvinyl alcohol); (iii) hybrid membrane [16–19]: to restrict the channel and induce a winding pathway for methanol transport by impregnating inorganic filler (e.g. zeolite, silica, montmorillonite and zirconium phosphate); (iv) surface modified membrane: to reduce the dissolution and/or block the transport of methanol by coating a metal layer (e.g. Pd and Pd–Ag alloy) [20–22] or methanol impermeable polymer layer (e.g. polyporphyrin, polybenzimidazole and polyvinyl alcohol) [23–25]. Among these methods, surface modification has been demonstrated as the commonly utilized approach because of its facile manipulation and high efficiency. Woo and co-workers [21] deposited Pd film on the surface of Nafion membrane using plasma etching and palladium-sputtering to reduce methanol crossover by about 35%. Kim et al. [22] developed a Pd particle-palladinized Nafion membrane through ion exchange followed by chemical reduction, and the Pd particles blocked the

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diffusion pathway for methanol, resulting in reduced methanol diffusion coefficient. However, besides the complex modification process, the presence of the modified layer usually increased the overall proton resistance. Various methanol barrier polymers have also been employed to inhibit methanol crossover. Hobson et al. [25] introduced a barrier layer of polybenzimidazole onto the Nafion surface to reduce the methanol permeability by about 40%. Hsing and co-workers [23] reported that the methanol crossover of Nafion membrane was significantly inhibited though coating a methanol impermeability polyvinyl alcohol film (the thickness about 1 μm) on Nafion surface. Unfortunately, the proton resistance in these cases was dramatically increased due to the existence of the relatively thick less-conductive layer (usually at micrometer scale) as well as the weak interfacial adhesion between the skin layer and Nafion layer [4,23,25]. Therefore, it is important to develop a facile approach to modify commercial Nafion membrane with a tightly attached ultrathin layer, which could effectively block the methanol transport channels without significantly affecting the proton transport.

Recent researches in biomaterials area found that dopamine, a kind of low-molecular-weight catecholamine mimics as the adhesive protein, could spontaneously self-polymerize on virtually all inorganic and organic surfaces and rapidly form a dense, ultrathin film under mild conditions [26–28]. Due to the strong physical and chemical interactions including hydrogen-bonding interaction, metal chelation, π–π interaction and electrostatic attractive interaction, the film layer was found to be homogenous and adhered tightly to the material surface [26]. Furthermore, numerous groups (amino, imino and catechol groups) were exposed to the polydopamine layer, which were proton conducting groups and with low ion resistance (about 1 Ω cm^{-2}), and hence it could be used as an ion-selective electrode [29]. We can thus conjecture that surface modification by coating polydopamine on Nafion membrane is likely to suppress methanol crossover remarkably and contribute to the high proton conductivity.

The objective of this study was to systematically examine the effect of dopamine coating conditions such as pH value, dopamine concentration and immersing time on the membrane performance including water uptake, swelling, methanol permeability and proton conductivity. Moreover, the physiochemical properties such as morphology, chemical structure, crystalline structures and free volume characteristics were investigated.

2. Experimental

2.1. Surface modification of Nafion membrane

The Nafion 117 membranes were supplied by DuPont. Prior to modification, the Nafion membranes were treated by boiling them sequentially for 1 h in each of the following solutions: de-ionized water, 3% H_2O_2 solution, de-ionized water, 1.0 M H_2SO_4 solution and de-ionized water. All treated membranes were stored in de-ionized water for the subsequent use.

A dilute, aqueous dopamine solution (2.0 mg ml^{-1}) was prepared by dissolving dopamine in tris(hydroxymethyl)aminomethane (Tris, Sigma–Aldrich, USA) solution. Hydrochloric acid (5.0 wt.%) was then added to adjust the pH values of the solution (7.5, 8.5 and 9.5). Next, the treated Nafion membranes were immersed directly into the dopamine solution with different pH values for 4 h at 20 ± 2 °C. The modified membranes were obtained after being washed with de-ionized water for 24 h. These modified membranes were designated as Naf–7.5, Naf–8.5 and Naf–9.5, corresponding to the pH values of dopamine solution.

The modified membranes at different dopamine concentrations were fabricated in the similar procedure. The treated Nafion membranes were immersed into different dopamine concentrations (1.0–4.0 mg ml^{-1}) under 8.5 of pH value for 4 h. These modified membranes were designated as Naf–1 mg, Naf–2 mg, Naf–3 mg and Naf–4 mg, corresponding to 1.0 mg ml^{-1}, 2.0 mg ml^{-1}, 3.0 mg ml^{-1} and 4.0 mg ml^{-1} of the dopamine concentration.

Similarly, the membranes were fabricated in 2.0 mg ml^{-1}, pH 8.5 dopamine solution for different times (from 1 h to 48 h). For simplicity, the resulting membranes were designated as Naf-X, where X (X = 1 h, 2 h, 4 h, 8 h, 12 h, 24 h, and 48 h) represented the immersing time.

2.2. Characterization

The cross-section of the membranes was observed using high resolution scanning electron microscope (HRSEM) Hitachi S4800 operated at 0.7 kV after being freeze-fractured in liquid nitrogen.

Fourier transform infrared spectra (FTIR, 4000–400 cm^{-1}) of the Nafion membranes before and after surface modification were recorded on a Nicolet-740 50X instrument.

The small-angle X-ray scattering (SAXS) and wide X-ray diffractometer (WXRD) were performed at a RigakuD/max2500v/Pc (CuK 40 kV, 200 mV) in the range of 0.1–7° and 3–60°, respectively. All the spectra were taken at ambient temperature (20 ± 2 °C). The peak position and its area were extracted with MDIjade5 software.

Positron annihilation lifetime spectroscopy (PALS) experiment was performed by using an EG&GORTEC fast–fast coincidence system (resolution 181 ps) at room temperature. The resource of ^{22}Na (5×10^5 Bq) was sandwiched between two pieces of sample, each with an overall thickness of about 0.2 mm. The integral statistics for each spectrum was more than 2×10^6 coincidences. In this technique, assuming that o-Ps was localized in a spherical potential well surrounded by an electron layer of thickness Δr equal to 0.1656 nm, the radius of free volume cavity (r) is obtained from pick-off annihilation lifetime (τ) of o-Ps in the free volume elements [30,31] by a semiempirical equation:

$$\tau = \frac{1}{2}\left[1 - \frac{\gamma}{\gamma + \Delta\gamma} + \left(\frac{1}{2\pi}\right)\sin\left(\frac{2\pi\gamma}{\gamma + \Delta\gamma}\right)\right]^{-1} \quad (1)$$

The volume of the equivalent sphere can be calculated by Eq. (2):

$$V_f = \frac{4\pi}{3}\gamma^3 \quad (2)$$

Further, the fractional free volume (FFV) may be estimated from Eq. (3):

$$\mathrm{FFV} = V_{f3}I_3 \quad (3)$$

where V_f and I are free volume of the sphere and intensity of o-Ps, respectively.

2.3. Water uptake and swelling

The water uptake of the membranes was determined as the following: the dry membrane was weighed (W_{dry}) and immersed in de-ionized water for 24 h at room temperature. Then the membrane was re-weighed (W_{wet}) quickly after removing the surface water. The surface swelling was determined in a similar manner, by soaking the dry rectangular membrane (about 4.0 cm × 4.0 cm) with area of A_{dry} in de-ionized water for 24 h, then re-measuring to obtain the wetted membrane area (A_{wet}). The final values of water uptake and swelling were the average of the three measurements with an error within ±5.0% and calculated by Eqs. (4) and (5), respectively:

$$\text{water uptake}\,(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (4)$$

$$\text{swelling}\,(\%) = \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100 \quad (5)$$

2.4. Methanol permeability

The methanol permeability was measured with a glass diffusion cell as described in the literature [32], which consisted of two compartments with identical volume separated by the membrane sheet. The membrane was hydrated in de-ionized water for 24 h before being clamped tightly between the two compartments, one of which was initially filled with water and the other filled with methanol solution (2 M or 12 M). The methanol concentration in the receipt compartment was determined using a gas chromatography (Agilent 6820) equipped with a TCD detector and a DB624 column. The methanol permeability, P ($\text{cm}^2\ \text{s}^{-1}$) was calculated from Eq. (6):

$$P = S\frac{V_B l}{AC_{A0}} \quad (6)$$

where S is the slope of the straight line of concentration versus time, V_B is the volume of the receipt compartment, l, A, and C_{A0} are the membrane thickness, effective membrane area, and feed concentration, respectively. The measurement error was within ±4.0%.

2.5. Proton conductivity

The proton conductivity of the membranes in the transverse direction was measured in two-point-probe conductivity cell by the ac impedance spectroscopy method over a frequency range of 10–10^6 Hz with oscillating voltage of 10 mV, using a frequency response analyzer (Compactstat, IVIUM Tech.) at 20 ± 1 °C. The two-point-probe conductivity cell was mainly composed of lower electrode (diameter: 3.0 cm) and upper electrode (diameter: 0.6 cm). Between these two electrodes, the membrane sample was sandwiched with the effective membrane area of 0.283 cm^2. All the membrane samples were immersed in de-ionized for 24 h prior to measurement. The proton conductivity (σ, S cm^{-1}) of the sample in transverse direction was calculated by Eq. (7):

$$\sigma = \frac{l}{AR} \quad (7)$$

where l and A are distance between the electrodes and effective membrane area, respectively, and R is the membrane resistance derived from the low intersect of the high frequency semicircle on a complex impedance plane with Re (z) axis.

3. Results and discussion

3.1. Surface modification of Nafion membrane

Fig. 1 shows the appearance of bare Nafion and modified Nafion membranes with different immersing times. It could be clearly seen from Fig. 1 that, with the increase of the immersing time, the color of Nafion membrane was changed from colorless (Fig. 1a) to dark-brown (Fig. 1b and c).

The cross-section micrographs of the modified membranes probed by HRSEM were shown in Fig. 2. The two-layer structure (polydopamine layer and Nafion layer) of the modified membranes could be seen clearly. HRSEM results showed that the polydopamine layer was dense and tightly adhered to the Nafion

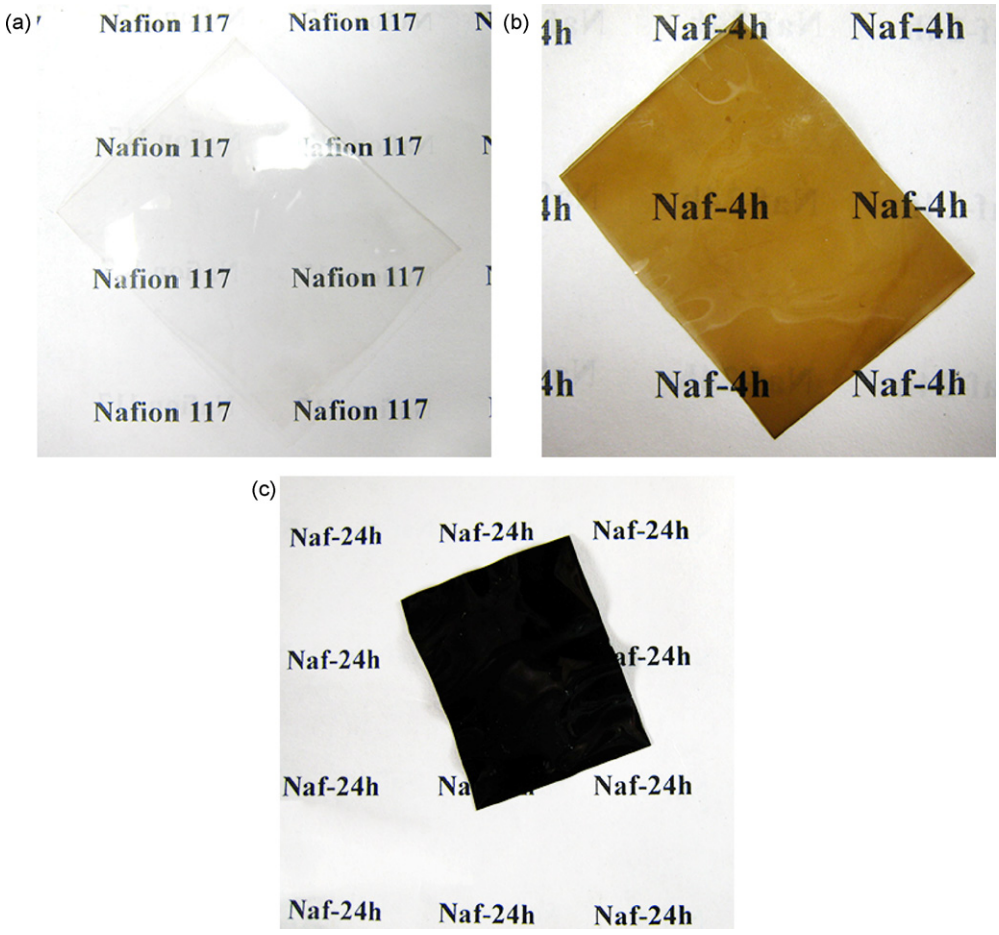

Fig. 1. The photographs of (a) Nafion, (b) Naf–4 h, and (c) Naf–24 h membranes.

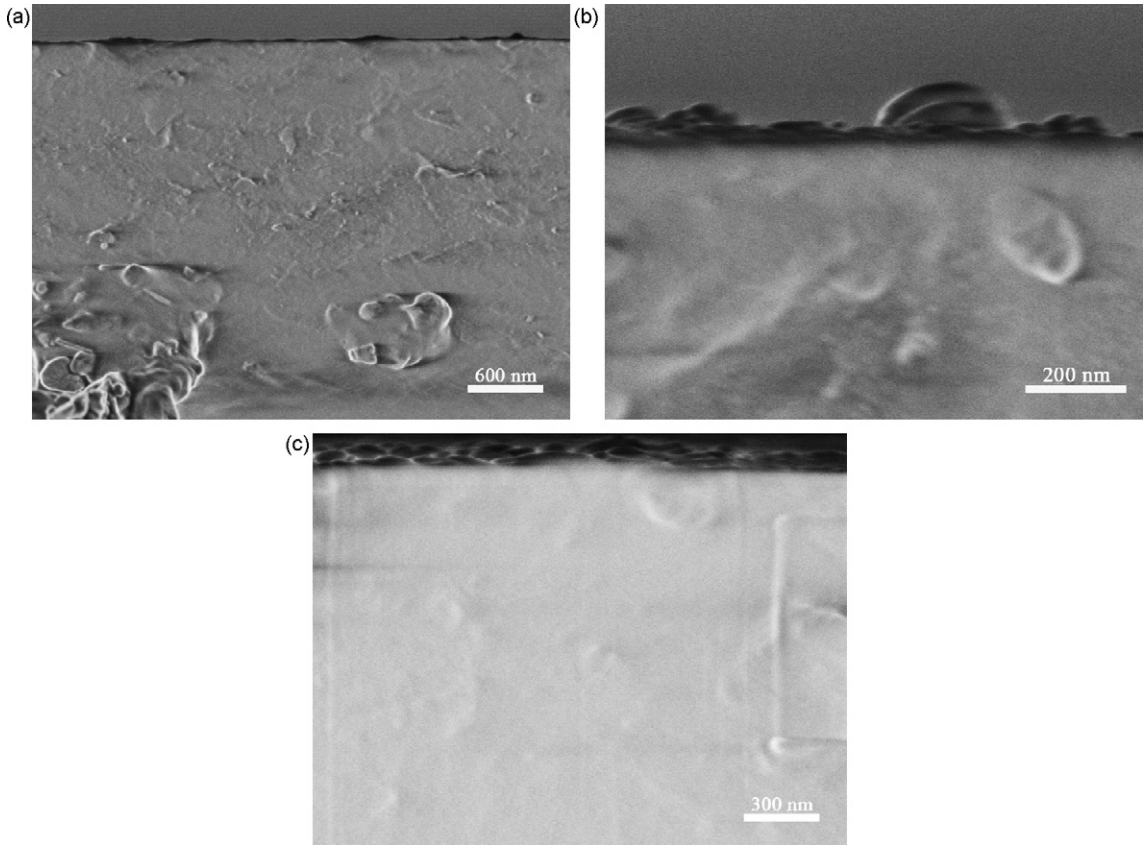

Fig. 2. HRSEM images of the cross-section of the membranes: (a and b) Naf–4 h on different scales and (c) Naf–24 h.

surface, and the thickness of this dense layer increased slightly (from 45 nm for Naf–4 h to 50 nm for Naf–24 h) with the immersing time. Granular particles were formed on the surface of the polydopamine layer, and the number and size of the particles increased with the immersing time, which was in good agreement with the observation in the literature [28]. Such phenomena can be tentatively explained as follows: at the beginning of polymerization, dopamine molecules were adsorbed on the Nafion surface due to the electrostatic interaction between sulfonic group of Nafion and amino group of dopamine. The dopamine monomers self-polymerized on the Nafion surface to form a dense layer with the aid of $-SO_3^-$ group, which facilitated the deprotonization of dopamine during polymerization process due to the high electron density of sulfonic group. With the increase of immersing time, the thickness of polydopamine layer increased and facilitation of $-SO_3^-$ group became less pronounced. Under this condition, dopamine molecules were inclined to polymerize on the rough sites owing to their high surface energy, and hence granular particles formed and grew on the nano-layer.

The chemical structure of the nano-layer was determined by FTIR as shown in Fig. 3. According to the spectra, the major vibrational fingerprints associated with the Nafion membrane could be found in all the samples. C–F stretching vibrations could be observed at 1208 cm^{-1} and 1153 cm^{-1}, and the peaks at 981 cm^{-1} and 969 cm^{-1} arised from the stretching vibration of C–O–C [33]. The typical peaks at 1056 cm^{-1} was assigned to the SO_3^- symmetric stretching vibration [33]. The existence of polydopamine after modification could be verified by the appearance of the absorbance peak at 1524 cm^{-1} which was attributed to N–H shearing vibration of the amide group and 1616 cm^{-1} corresponding to the overlap of C=C resonance vibration in aromatic ring and N–H bending (Fig. 3b–d). HRSEM and FTIR results revealed that a dense nano-layer was formed by self-polymerization of dopamine and adhered tightly on Nafion surface, which rendered the possibility to inhibit the methanol crossover of Nafion membrane by substantially blocking the ion-cluster channels for methanol transport.

3.2. Microstructure characterization of the membranes

Since the mass transport in Nafion-based membranes can be described by solution-diffusion mechanism, the microstructure would strongly influence the membrane performance in terms of methanol permeability and proton conductivity [8,9]. The

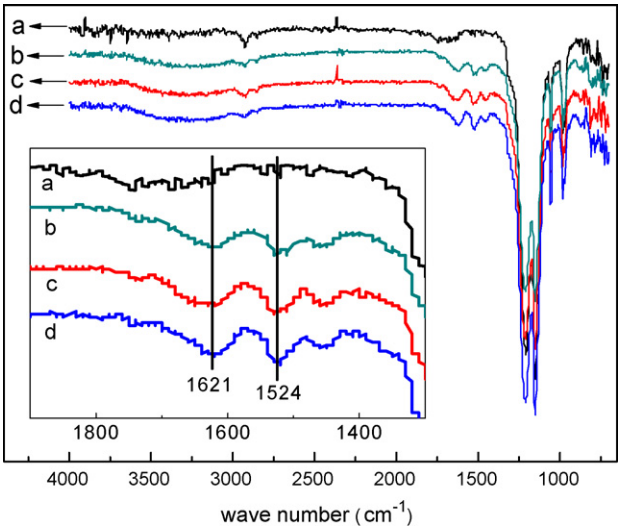

Fig. 3. FTIR spectra of the membranes: (a) Nafion, (b) Naf–1 h, (c) Naf–4 h, and (d) Naf–24 h membranes.

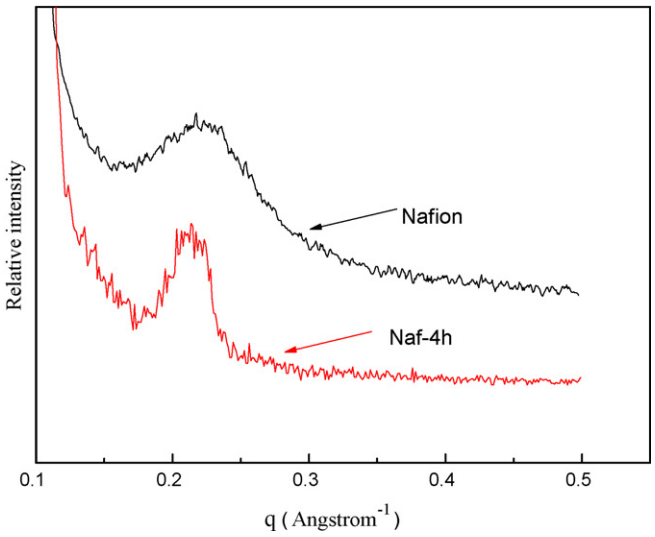

Fig. 4. SAXS curves of Nafion membranes before and after modification.

internal morphologies of the membranes including crystalline structure were determined by SAXS and WXRD and free volume characteristics were investigated by PALS, respectively.

Fig. 4 shows the relative scattering intensity of the dried control and modified Nafion membranes as a function of the scattering vector q, where $q = 4\pi/\lambda \sin\theta$ with the scattering angle 2θ and the X-ray wavelength λ. The scattering maximum generally appeared in scattering vector profiles at around ca. $q = 0.2$ Å^{-1} (the well-known "ionomer peak"), which related to the characteristic correlation length of the domains in which the water was contained [34,35]. By comparing the SAXS curves of Nafion and Naf–4 h, it was found that both the position and intensity of the ionomer peak were little changed after modification. This implied that the inter-cluster distance for the two-phase model or the short-range distance for the core–shell model was largely preserved after surface modification, which were in consistence with the results in the literature [36].

Fig. 5 presents the WXRD patterns of control and modified Nafion membranes. All the membranes exhibited the same broad characteristic peaks at 2θ = 12–20° and 2θ = 35–45° [37,38]. The former broad diffraction peaks (1 0 0) resulted from a convolution of amorphous (2θ = 16°) and crystalline (2θ = 17.5°) scattering

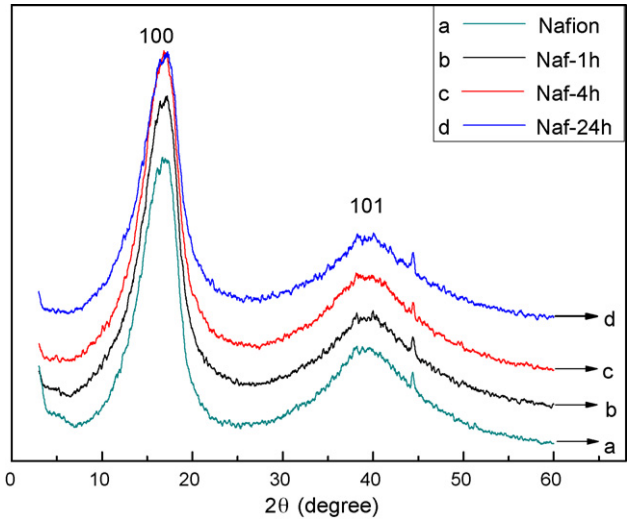

Fig. 5. WXRD patterns of (a) Nafion, (b) Naf–1 h, (c) Naf–4 h, and (d) Naf–24 h membranes.

Table 1
Free volume parameters of Nafion before and after modification.

Entry	Membrane	τ_3 (ns)	I_3 (%)	r_3 (nm)	V_f (nm^3)	FFV (%)
1	Nafion	2.535	13.57	0.3295	0.1498	4.475
2	Naf–7.5	2.563	12.70	0.3316	0.1527	4.211
3	Naf–8.5	2.334	13.38	0.3134	0.1289	4.193
4	Naf–9.5	2.445	13.15	0.3233	0.1415	4.251
5	Naf–1 mg	2.386	13.86	0.3178	0.1344	4.405
6	Naf–2 mg	2.37	13.80	0.3165	0.1327	4.367
7	Naf–3 mg	2.427	13.40	0.3211	0.1386	4.302
8	Naf–4 mg	2.412	13.41	0.3199	0.1371	4.289
9	Naf–1 h	2.429	13.49	0.3212	0.1387	4.333
10	Naf–2 h	2.551	13.01	0.3307	0.1514	4.299
11	Naf–4 h	2.427	13.44	0.3211	0.1386	4.316
12	Naf–8 h	2.493	12.93	0.3263	0.1455	4.219
13	Naf–12 h	2.448	12.98	0.3227	0.1407	4.189
14	Naf–24 h	2.409	13.24	0.3197	0.1368	4.233
15	Naf–48 h	2.486	12.80	0.3257	0.1447	4.169

from the perfluorocarbon chains of Nafion. The later peaks (1 0 1) were attributed to the crystalline –[CF_2–CF_2]– of Nafion. The results in Fig. 5 indicated that the position and intensity of the characteristic peaks for membranes were slightly changed after surface modification, which agreed with the literature observations [39]. In summary, SXAS and WXRD results implied the similar morphologies of Nafion layer for both control and modified Nafion membranes, therefore methanol molecules transported still predominantly through the ion-cluster channels in Nafion layer.

Free volume characteristics of the prepared membranes were also investigated to get a deeper understanding of the material microstructure, which were reported as an effective direct datum for describing membrane morphology [30]. PALS technique, as a unique and direct way, was employed to probe the free volume of the membranes, in which the o-Ps was assumed to pass throughout the sample for displaying the property of the whole material [30,31]. Since the thickness of the nano-layer (around 50 nm) was much thinner than that of Nafion layer (around 180 μm), the free volume parameters obtained by PALS mainly reflected the microstructure of Nafion layer. According to the r_3 parameter in Table 1, the average size of the cavities kept almost unchanged after (Entries 2–15) modification. These results demonstrated that dopamine molecules mainly polymerized on the Nafion surface, and the internal microstructure of Nafion layer was little affected, as testified by the characterization of SAXS and WXRD. On the other hand, the average free volume cavity radius (around 0.32 nm) was larger than the kinetic radius of methanol molecule (0.19 nm), and thus methanol transporting through the membrane might occur in free volume cavities. The fractional free volume (FFV parameter in Table 1) of the modified Nafion membranes (Entries 2–15) was smaller than that of control Nafion membrane (Entry 1), which was advantageous to suppress methanol crossover of the membranes (as discussed hereafter).

3.3. *Effect of modification conditions upon the membrane performance*

3.3.1. *Effect of pH value*

Since the self-polymerization of dopamine was carried out under weak alkaline condition [26], the influence of pH value of dopamine solution upon the membrane performance including water uptake, swelling, methanol permeability and proton conductivity was measured in the range of 7.5–9.5. Table 2 demonstrates that the modified Nafion membranes displayed lower water uptake (Entries 2–4, about 25%) and swelling (Entries 2–4, about 30%) compared with control Nafion membrane (Entry 1, 31% for water uptake and 38% for swelling). The possible assumptions were presented as follows: (i) polydopamine was hydrophobic comparing to

Table 2
Water uptake, swelling and selectivity of control membrane and Nafion membranes modified under different pH values.

Entry	Membrane	Water uptake (%)	Swelling (%)	Selectivity ($\times 10^{-4}$ S s cm^{-3})	
				2 M[a]	12 M[a]
1	Nafion	30.55	37.56	2.20	1.73
2	Naf–7.5	24.49	28.55	9.54	5.47
3	Naf–8.5	23.82	24.64	9.97	5.15
4	Naf–9.5	27.64	32.87	7.76	4.39

[a] Selectivity ($S = \sigma/P$) of the membrane was calculated from the proton conductivity σ and methanol permeability P. 2 M refers to the selectivity of 2 M methanol solution, that is, the methanol permeability (P) was obtained in 2 M methanol solution, and 12 M refers to the selectivity of 12 M methanol solution.

perfluorosulfonic acid of Nafion, and thus the modification would decrease the hydrophilicity of the membrane; (ii) although the polymerization mechanism of dopamine was still elusive presently [27,28,40,41], it was accepted that the catechol groups were firstly oxidized to the quinones which further participated in intramolecular cyclization and a variety of inter-molecules cross-linking reactions. The resulting network structure of polymerization layer would inhibit membrane swelling and reduce fractional free volume as summarized in Table 1 [42]. According to the results in Table 2 (Entries 2–4), the Naf–8.5 membrane displayed lower water uptake and swelling comparing to Naf–7.5 and Naf–9.5 membranes probably due to its lower fractional free volume.

Methanol permeability of Nafion membranes before and after surface modification in 2 M and 12 M aqueous methanol solution was illustrated in Fig. 6. In agreement with the literatures [32,43], the methanol crossover of Nafion-based membranes in 2 M methanol solution was lower than that in 12 M methanol solution, and such phenomena were reasonably due to the properties of aqueous methanol solution and the microstructure of the Nafion-based membrane [32]. According to Fig. 6, the methanol barrier property of Nafion membrane was significantly improved by about 75% through surface modification of dopamine. The considerable improvement was probably ascribed to the facts that: (i) the reduction of the hydrophilicity of membrane surface after modification would decrease the dissolution of methanol molecules; (ii) the presence of polydopamine nano-layer simultaneously blocked the channels on the Nafion surface and decreased the size of the internal channels by suppressing membrane swelling, and consequently enhanced methanol diffusion resistance. Based on previous studies [44,45], pH value had two different influences on the self-polymerization of dopamine: (i) the polymerization rate increased

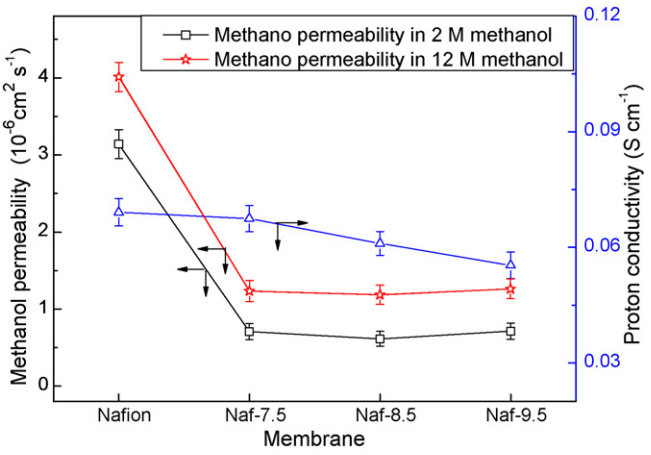

Fig. 6. The methanol permeability and proton conductivity of control membrane and Nafion membranes modified under different pH values.

with the increase of pH value from 7.5 to 9.5, and therefore more polydopamine was formed at a definite time interval; (ii) the ratio of quinone structure to catechol structure of polydopamine was also increased, which would induce a looser structure. Naf–8.5 membrane, which was prepared under pH 8.5, possessed moderate polymerization rate and polymer structure. The resulting polydopamine layer might induce lower fractional free volume (FFV parameter in Table 1) and consequently endow lower methanol crossover comparing to that of Naf–7.5 and Naf–9.5 membranes. Meanwhile, this pH value was essentially similar to the pH of sea water (8.2–8.4), in which dense polydopamine film was formed by mussels and other marine organisms.

Proton conductivity of Nafion membrane at room temperature under water immersed conditions was 0.069 S cm^{-1}, which agreed with the result obtained in the literatures [19,32]. The proton conducting ability of polydopamine was lower than that of perfluorosulfonic acid, however, the proton conductivity of the Nafion membrane was decreased only slightly after surface modification as shown in Fig. 6. The high value was possibly ascribed to the facts that: on one hand, the proton conducting groups (e.g. amino, imino and catechol groups) of polydopamine layer would facilitate proton transport; on the other hand, the nano-layer was too thin comparing with Nafion layer (about 1/3500) to affect proton conductivity. As pH value increased, the polymerization rate as well as the ratio of quinone structure to catechol structure increased, both of which enhanced the resistance of proton transport through the polydopamine layer. Accordingly, proton conductivity of the modified membrane reduced with higher pH value, as illustrated in Fig. 6.

The comprehensive performance of the membrane was reflected by selectivity S, where $S = \sigma/P$ with the proton conductivity σ and methanol permeability P [16]. As shown in Table 2 (selectivity parameter), the selectivity of the membranes was dramatically improved through surface modification of dopamine. Nano-layer of polydopamine may have more influence on methanol transport than that on proton transport. Meanwhile, since the radius of methanol molecule was larger than that of proton, the reduction of the channels size of Nafion layer would enhance much more diffusion resistance for methanol molecules than that for protons. Therefore, the modified membranes displayed much higher selectivity than control Nafion membrane. Owing to the excellent methanol barrier property, the Naf–8.5 exhibited the highest comprehensive performance among the modified membranes under different pH values.

3.3.2. *Effect of immersing time*

Since the highest comprehensive performance of the membrane was acquired under pH 8.5, the effect of immersing time from 1 h to 48 h on membrane performance was experimented under such pH value, and the results were summarized in Table 3 and Fig. 7. As shown in Table 3, the water uptake of modified Nafion membranes with different immersing times was little changed in the range of 23–25%. The swelling caused by the adsorption of water was quite consistent with the results of water uptake with little changed in the range of 24–26%.

Lee et al. [44] found that the pH value of aqueous solution determined the structure of polydopamine layer via tailoring the ratio of quinone structure to catechol structure. The immersing time and dopamine concentration would primarily influence the thickness of the polydopamine layer and therefore manipulate the membrane performance. Fig. 7 presents the methanol permeability and proton conductivity of control and modified Nafion membranes with different immersing times. According to HRSEM analysis, the thickness of dense nano-layer was around 50 nm and kept almost unchanged with the immersing time under certain pH value and concentration. As shown in Fig. 7, the methanol permeability in both 2 M and

Table 3
Water uptake, swelling and selectivity of control membrane and Nafion membranes modified with different immersing times.

Entry	Membrane	Water uptake (%)	Swelling (%)	Selectivity ($\times 10^{-4}$ S s cm^{-3})	
				2 M[a]	12 M[a]
1	Nafion	30.55	37.56	2.20	1.73
2	Naf–1 h	23.08	23.87	9.87	4.67
3	Naf–2 h	24.47	25.31	11.41	4.54
4	Naf–4 h	23.82	24.63	9.97	5.15
5	Naf–8 h	23.99	24.82	12.01	4.97
6	Naf–12 h	23.38	24.19	10.19	5.59
7	Naf–24 h	23.21	24.01	9.13	5.29
8	Naf–48 h	23.86	24.68	9.26	4.77

[a] Selectivity ($S = \sigma/P$) of the membrane was calculated from the proton conductivity σ and methanol permeability P. 2 M refers to the selectivity of 2 M methanol solution, that is, the methanol permeability (P) was obtained in 2 M methanol solution, and 12 M refers to the selectivity of 12 M methanol solution.

12 M aqueous methanol solution of the modified membranes was much lower than that of control Nafion membrane but changed only slightly with the immersing time. Similarly to methanol permeability, the proton conductivity (around 0.06 S cm^{-1}) of the membranes was little changed with the immersing time. Based on the improvement of methanol barrier property, all the modified membranes exhibited improved selectivity about five times of that of control Nafion membrane. All these results indicated that the effect of the surface modification upon membrane performance was mainly dependent on the dense nano-layer, which could suppress membrane swelling and block the channels on the Nafion surface effectively.

3.3.3. *Effect of dopamine concentration*

Considering the comprehensive performance, the effect of dopamine concentration from 1 mg ml^{-1} to 4 mg ml^{-1} upon membrane performance was investigated under pH 8.5 for 4 h. According to Table 4, surface modification reduced the water uptake (from 31% to less than 25%) and swelling (from 38% to less than 28%), and such trends decreased slightly with the increase of dopamine concentration from 1 mg ml^{-1} to 4 mg ml^{-1}.

The methanol permeability and proton conductivity of control membrane and Nafion membranes modified at different dopamine concentrations were presented in Fig. 8. The methanol crossover of the modified Nafion membranes was about 25% of that of control Nafion membrane. Similar to the trend of water uptake, the methanol permeability also decreased slightly by about 15% independently with the dopamine concentration in the range of

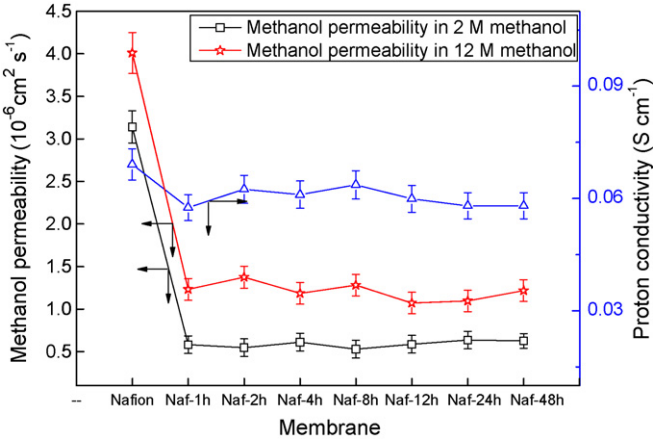

Fig. 7. The methanol permeability and proton conductivity of control membrane and Nafion membranes modified with different immersing times.

Table 4
Water uptake, swelling and selectivity of control membrane and Nafion membranes modified at different dopamine concentrations.

Entry	Membrane	Water uptake (%)	Swelling (%)	Selectivity ($\times 10^{-4}$ S s cm^{-3})	
				2 M[a]	12 M[a]
1	Nafion	30.55	37.56	2.20	1.73
2	Naf–1 mg	25.36	27.60	9.09	4.69
3	Naf–2 mg	23.83	24.64	9.97	5.15
4	Naf–3 mg	23.53	23.69	9.77	5.04
5	Naf–4 mg	22.82	22.56	10.59	5.47

[a] Selectivity ($S = \sigma/P$) of the membrane was calculated from the proton conductivity σ and methanol permeability P. 2 M refers to the selectivity of 2 M methanol solution, that is, the methanol permeability (P) was obtained in 2 M methanol solution, and 12 M refers to the selectivity of 12 M methanol solution.

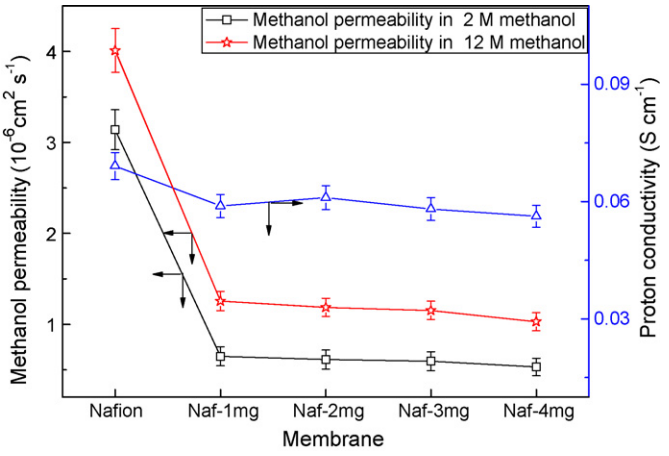

Fig. 8. The methanol permeability and proton conductivity of control membrane and Nafion membranes modified at different dopamine concentrations.

1–4 mg ml^{-1}. Proton conductivity of modified Nafion was only a little lower than that of control Nafion membrane. These inapparent changes indicated that the increase of thickness of the nano-layer was inappreciable comparing with the whole membrane as the dopamine concentration increased under certain pH value and immersing time. Due to weak influence of dopamine concentration on methanol permeability and proton conductivity, the selectivity of the modified Nafion membranes was slightly changed (about 9.5 and 5.3 for 2 M and 12 M methanol, respectively) as shown in Table 4.

4. Conclusion

Commercial Nafion membranes have been modified through mild and rapid self-polymerization of dopamine, a kind of low-molecular-weight catecholamine mimics. A dense polydopamine nano-layer was quickly formed and tightly resided on the Nafion surface, which dramatically influenced the membrane performance. Since only few monomers were penetrated into Nafion layer, the microstructure of Nafion was hardly affected. The network structure of polydopamine layer would suppress membrane swelling, and thus decreased the size of ion-cluster channels and fractional free volume, which both facilitated to inhibit the methanol crossover of the membranes from 3.14×10^{-6} cm^2 s^{-1} to about 0.65×10^{-6} cm^2 s^{-1}. Due to the presence of numerous proton conducting groups within the ultrathin polydopamine layer, the proton conductivity of the Nafion membrane decreased only slightly after modification. Nafion membrane modified under pH 8.5 (similar to the pH value of sea water environment) possessed moderate polymerization rate and polymer structure, and

consequently endowed the superior performance to the membranes modified under other pH values. The effect of dopamine concentration and immersing time upon methanol permeability and proton conductivity was not significant, as the thickness of the polydopamine layer was inappreciable compared with the whole membrane under different dopamine solution concentrations and immersing times. It is deserved to highlight the methanol barrier property and comprehensive performance of Nafion membranes which were significantly enhanced through this facile surface modification technique, which proved their high potential for DMFC applications.

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References

[1] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Chem. Mater. 15 (2003) 4896–4905.
[2] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587–4612.
[3] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Shin, J.S. Kim, J. Power Sources 118 (2003) 205–211.
[4] S.P. Jiang, Z. Liu, Z.Q. Tian, Adv. Mater. 18 (2006) 1068–1072.
[5] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, J. Power Sources 83 (1999) 204–216.
[6] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466–474.
[7] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.
[8] K.D. Kreuer, S.J. Paddison, E. Spohr, M. Schuster, Chem. Rev. 104 (2004) 4637–4678.
[9] F.N. Büchi, G.G. Scherer, J. Electrochem. Soc. 148 (2001) A183–A188.
[10] C. Schmidt, T. Glück, G. Schmidt-Naake, Chem. Eng. Technol. 31 (2008) 13–22.
[11] V. Tricoli, J. Electrochem. Soc. 145 (1998) 3798–3801.
[12] G. Suresh, A.K. Pandey, A. Goswami, J. Membr. Sci. 295 (2007) 21–27.
[13] N.W. DeLuca, Y.A. Elabd, J. Power Sources 163 (2006) 386–391.
[14] K.Y. Cho, J.Y. Eom, H.Y. Jung, N.S. Choi, Y.M. Lee, J.K. Park, J.H. Choi, K.W. Park, Y.E. Sung, Electrochim. Acta 50 (2004) 583–588.
[15] Q.M. Huang, Q.L. Zhang, H.L. Huang, W.S. Li, Y.J. Huang, J.L. Luo, J. Power Sources 184 (2008) 338–343.
[16] Z. Chen, B. Holmberg, W. Li, X. Wang, W. Deng, R. Munoz, Y. Yan, Chem. Mater. 18 (2006) 5669–5675.
[17] F. Bauer, M. Willert-Porada, Fuel Cells 6 (2006) 261–269.
[18] Y.F. Lin, C.Y. Yen, C.C.M. Ma, S.H. Liao, C.H. Lee, Y.H. Hsiao, H.P. Lin, J. Power Sources 171 (2007) 388–395.
[19] C.H. Rhee, H.K. Kim, H. Chang, J.S. Lee, Chem. Mater. 17 (2005) 1691–1697.
[20] Z.Q. Ma, P. Cheng, T.S. Zhao, J. Membr. Sci. 215 (2003) 327–336.
[21] W.C. Choi, J.D. Kim, S.I. Woo, J. Power Sources 96 (2001) 411–414.
[22] Y.J. Kim, W.C. Choi, S.I. Woo, W.H. Hong, Electrochim. Acta 49 (2004) 3227–3234.
[23] Z.G. Shao, X. Wang, I.M. Hsing, J. Membr. Sci. 210 (2002) 147–153.
[24] A. Bettelheim, L. Soifer, E. Korin, J. Electroanal. Chem. 571 (2004) 265–272.
[25] L.J. Hobson, Y. Nakano, H. Ozu, S. Hayase, J. Power Sources 104 (2002) 79–84.
[26] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Science 318 (2007) 426–430.
[27] H. Lee, J. Rho, P.B. Messersmith, Adv. Mater. 20 (2008) 1–4.
[28] J.H. Waite, Nat. Mater. 7 (2008) 8–9.
[29] R. Zeng, Z. Pang, H. Zhu, J. Electroanal. Chem. 490 (2000) 102–106.
[30] P. Winberg, K. DeSitter, C. Dotremont, S. Mullens, I.F.J. Vankelecom, F.H.J. Maurer, Macromolecules 38 (2005) 3776–3782.
[31] M. García, J. Barsema, R.E. Galindo, D. Cangialosi, J. Garcia-Turiel, W.E. van Zyl, H. Verweij, D.H.A. Blank, Polym. Eng. Sci. 44 (2004) 1240–1246.
[32] J. Wang, X. Zheng, H. Wu, B. Zheng, Z. Jiang, X. Hao, B. Wang, J. Power Sources 178 (2008) 9–19.
[33] M.A. Smit, A.L. Ocampo, M.A. Espinosa-Medina, P.J. Sebastián, J. Power Sources 124 (2003) 59–64.
[34] K. Schmidt-Rohr, Q. Chen, Nat. Mater. 7 (2008) 75–83.
[35] A. Saccà, A. Carbone, R. Pedicin, G. Portale, L. D'Ilario, A. Longo, A. Martorana, E. Passalacqua, J. Membr. Sci. 278 (2006) 105–113.
[36] L. Rubatat, O. Diat, Macromolecules 40 (2007) 9455–9462.
[37] F. Bauer, M. Willert-Porada, J. Membr. Sci. 233 (2004) 141–149.
[38] W. Howard Jr., Starkweather, Macromolecules 15 (1982) 320–323.
[39] X. Liu, C. Suo, Y. Zhang, X. Wang, C. Sun, L. Li, L. Zhang, J. Micromech. Microeng. 16 (2006) S226–S232.
[40] A. Pezzella, L. Panzella, A. Natangelo, M. Arzillo, A. Napolitano, M. d'Ischia, J. Org. Chem. 72 (2007) 9225–9230.
[41] E. Kaxiras, A. Tsolakidis, G. Zonios, S. Meng, Phys. Rev. Lett. 97 (2006) 218102.
[42] A. Lee, Ph.D. Thesis, Northwestern University, USA, 2005.
[43] V.M. Barragán, C. Ruiz-Bauzá, J.P.G. Villaluenga, B. Seoane, J. Power Sources 130 (2004) 22–29.
[44] H. Lee, N.F. Scherer, P.B. Messersmith, Proc. Natl. Acad. Sci. 103 (2006) 12999–13003.
[45] C. Foppoli, R. Coccia, C. Cini, M.A. Rosei, Biochim. Biophys. Acta 1334 (1997) 200–206.