Carbon dots with multi-functional groups and the application in proton exchange membranes

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ARTICLE INFO
Article history:
Received 8 September 2017  
Received in revised form  
24 October 2017  
Accepted 7 November 2017  
Available online 8 November 2017

Keywords:
Carbon dots  
Nafion  
Multi-functional groups  
Proton exchange membrane

ABSTRACT
It is of great necessity to achieve a proton exchange membrane (PEM) with high proton conductivity and low methanol permeability for the practical applications. Nafion modified carbon dots (NCDs) with multi-functional groups were successfully synthesized via the pyrolysis of citric acid (CA) with the existence of Nafion. The modification process is motivated by the hydrophilicity-to-hydrophobicity transformation of CA as well as the non-covalent hydrophilic-hydrophobic interaction during the pyrolysis procedure. Multi-functionalized NCDs with moderate hydrophilicity influence the aggregation structure of Nafion matrix of the composite membranes and effectively enhance the high-temperature water retention ability. Both the proton conductivity and the methanol resistance ability of the composite PEMs are significantly enhanced. 0.5-NCD-0.5 Nafion composite PEM presents a 5–10 times increase in proton conductivity and 50% percent decrease in methanol permeability than that of recast Nafion.

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1. Introduction
Proton exchange membrane (PEM) is an important constituent part of the direct methanol fuel cells (DMFC) to transport protons and impede fuel [1]. It is of great necessity to achieve a high-performance PEM with high proton conductivity and low methanol permeability. Unfortunately, methanol molecules and protons use the same transportation channels in the polymer membrane matrix so that there is a “trade-off” effect between proton conductivity and methanol resistance, which means the proton conductivity probably decreases when the methanol permeability is tried to be suppressed [2,3]. Perfluorosulfonic acid polymer, Nafion, is a representative PEM material with good stability and high proton conductivity at optimal water contents [4,5]. However, high methanol permeability of Nafion badly hinders the extensive industrialization of DMFC [6].

Functionalized nanomaterials have been widely used in the modification of PEMs. The nanomaterials with hydrophilic oxygen-containing groups (–OH, –COOH, etc.) are usually utilized to promote the water retention ability of the composite membranes and facilitate the proton conduction at high-temperature conditions [6–9]. Nanomaterials with sulfonic groups (–SO3H) were intensely used to increase the proton conductivity [10,11]. The sulfonic groups could create more proton transportation sites in the membrane matrix and adjust the aggregation structure of Nafion matrix to form more connected proton nanochannels [12]. The geometric morphology and methanol resistant property of the nanomaterials (GO, CNT, etc.) were employed to lower the methanol permeability of the composite membranes [13–15]. However, it is very challenging to adopt the nanomaterials with single functional groups to promote the various performance of Nafion. Recently, it has been reported by Wang group that the proton conduction among –SO3H groups and –COOH groups has a lower energy barrier than that among –SO3H groups [16]. Thus, the proton conductivity is increased with the co-existence of –SO3H groups and –COOH groups. This inspired us to design a hydrophilic nanofiller with multiple functional groups including highly acidic –SO3H groups, weakly acidic –COOH groups and methanol resistant part to improve both proton conductivity and methanol resistance of PEMs.

Carbon dots (CDs), as a new kind of carbon nanomaterials, are usually referred to small carbon nanoparticles of less than 10 nm. CDs have aroused intense research interest on account of their unique properties such as broadband optical absorption,
photoluminescence, chemical inertness, low toxicity, etc. [17–19]. It is convenient to achieve functionalized CDs via bottom-up method by blending small molecules or polymers with specific functional groups with the CD precursors. This largely enriches the functions and applications of CDs. Citric acid (CA) is a promising carbon source for bottom-up CD synthesis method benefitting from its low cost, abundant sources and low carbonization temperature (<200 °C) to avoid the degradation of the functionalization reagents. Besides, CDs achieved from CA also possess plenty oxygen-containing groups (−COOH, −OH, etc.) on the periphery and present excellent hydrophilicity [18]. Dong et al. chose CA as the carbon source and branched polyethyleneimine (BPEI) as the functionalization reagent to successively synthesize BPEI-functionalized CDs which showed promising applications in chemical sensing [19]. Zhai et al. used various amine molecules including 1,2-ethylenediamine, diethylamine, and trimethylamine as N-doping precursors and surface passivation agents to prepare functionalized CDs [20]. Bhattacharjee et al. reported poly (4-styrene sulphonate)-stabilized carbon quantum dots via the similar method [21]. Compared with other nanomaterials, microscopically CDs with multi-functional groups possess the comparable size of the (−SO3)ionic clusters in Nafion. This advantage might bestow CDs with a different impact on the aggregation structure as well as the crystalline behavior of Nafion during the membrane-forming process. However, as far as we know, limited works about enhancing proton exchange membranes with CDs or functionalized CDs have been reported. Malik et al. first synthesized functionalized CdSe quantum dots (FQDs) with −COOH and −SO3H groups via the ligand exchange method. Then the FQDs were blended with poly (vinyl alcohol) (PVA) to prepare PVA/FQD cross-linked PEMs, whose proton conductivity achieved 10−2 S cm−1 from 25 to 70 °C at 100% relative humidity [22]. Hence, it arouses our keen interest to design a multi-functionalized CD and investigate its influences on the composite PEMs.

Herein, citric acid (CA) was chosen as the carbon source for its low pyrolysis temperature (<200 °C) to avoid degradation of the functionalization reagent, Nafion. Nafion modified carbon dots (NCDs) with multi-functional groups originated from CA and Nafion were first synthesized via a low-temperature bottom-up method by exploiting the hydrophilic-hydrophobic transformation of CA during the carbonization process. The influences of the different ratio between Nafion and CA on the obtained NCDs were investigated as well. NCDs are bestowed with various functions including high water retention ability, active proton transportation spots, good interaction with Nafion matrix and methanol resistance. Then the NCDs were blended with Nafion to prepare NCD Nafion composite PEMs. NCDs with −COOH and −SO3H functional groups have an impact on the aggregation structure of the composite PEMs during the membrane-forming process via the hydrophilic and H-bonding interaction. Benefiting from the unique properties of NCDs, NCD Nafion composite PEMs present a significant increase in proton conductivity under various conditions. At the meantime, the hydrophobic polytetrafluoroethylene backbone of Nafion makes the NCDs repel methanol molecules to restrain the methanol crossover phenomenon in the composite PEMs.

2. Experimental materials and methods

2.1. Materials

Citric acid (CA) was obtained from Aladdin Co. (China). Nafion solution (perfluorinated resin solution, 5 wt%) was purchased from Sigma-Aldrich. Nafion 117 is bought from 3 M Co. H2SO4, H2O2 and N, N-dimethyl formamide (DMF) were acquired from Sinopharm Chemical Reagent Co. (China). All the chemical reagents were used as received.

2.2. Synthesis of NCDs

The synthesis procedure was referred to the previous report [21]. Typically, 2 mL 5 wt% Nafion solution was added into 20 mL 1.5 wt% CA aqueous solution. The mixed solution was freeze-dried after being ultrasonicated for 30 min. The freeze-dried mixture was then put into a tubular furnace and pyrolyzed at 200 °C for 2 h under N2 atmosphere, and the obtained product was dialyzed for purification. After filtration and freeze-drying, the functionalized CDs were finally achieved and named as NCD-0.3 while the number 0.3 represents the mass ratio of Nafion and citric acid (CA) in the precursor mixture (Table S1). Similarly, NCD-0.5 and NCD-1 were synthesized via the same method except that the concentration of the CA aqueous solution was 1 wt% and 0.5 wt%, respectively. CD was also synthesized via the similar method where the as-received CA powder was directly pyrolyzed.

2.3. Preparation of NCD Nafion composite PEMs

The composite PEM preparation process was similar to our previous report [23]. Briefly, 4 mL 5 wt% Nafion solution was first exchanged with 3 mL DMF by rotary evaporation. Then 1 mL 1 mg/ mL NCD-0.3 DMF dispersion was added into the Nafion DMF solution. Second, the obtained dispersion was cast onto a glass mold in a vacuum oven. Third, the acquired membrane was treated with 3 wt% H2O2 solution and 1 M H2SO4 solution. The finally obtained composite membrane was named as 0.5-NCD-0.3 Nafion, where 0.5 means the weight percentage of NCD-0.3 in Nafion matrix. Other composite PEMs were prepared and named similarly. Recast Nafion was also prepared for comparison.

2.4. Characterization of CD and NCDs

High-resolution transmission electron microscopy (HR-TEM) images were taken on JEM-2100F (JEOL) with an acceleration of 200 kV to observe the morphology of NCDs. X-ray photoelectron spectra (XPS) were achieved on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Ka radiation. The Fourier transform infrared spectroscopy (FTIR) spectra were acquired on a NEXUS 6700 spectrometer (Thermofisher) with a resolution of 4 cm−1 and 64 scans. The fluorescence spectra (FLS) were taken on a RF-5301PC spectrometer (Shimadz).

2.5. Characterization of PEMs

The field-emission scanning electron microscope (FE-SEM) images were taken on Ultra 55 (Zeiss) at a working voltage of 3 kV. All the PEMs were sprayed with gold before observation. The atomic force microscope (AFM) images of the PEMs were obtained on Multimode 8 (Bruker) in peak force QNM imaging mode. The thermal degradation was investigated on TGA 1 Thermo Gravimetric Analyzer (Mettler Toledo) under N2 atmosphere (heating rate of 20 °C min−1). The FTIR spectra were recorded using NEXUS 6700 (Thermofisher) with an ATR attachment with a resolution of 4 cm−1 and 64 scans. The crystalline behavior of the PEMs was studied via the X-ray diffraction (XRD) analyses conducted on PANalytical X’pert diffractometer with Cu Kα radiation. The data analyses were referred to the previous report [24]. The mechanical test was conducted on SANS universal testing machine (Shenzhen, China). The water uptake (HU) values of the PEMs at 30 and 100 °C were measured similarly as our earlier report with equation (1):
where $W_{wet}$ is the weight of the wet PEM and $W_{dry}$ is the weight of the dry PEM. The swelling ratio (SW) in water at 30 °C was acquired from equation (2):

$$SW(\%) = \frac{S_{wet} - S_{dry}}{S_{dry}} \times 100\%$$  \hspace{1cm} (2)$$

where $S_{wet}$ is the area of the wet PEM and $S_{dry}$ is the area of the dry PEM. The proton conductivity experiments were undertaken on a CHI660E electrochemical workstation via a four electrode method under AC Impedance mode (0.1 MHz – 1 Hz). All the PEMs were placed in a BPHJ-120AF temperature and humidity test chamber (Shanghai Bluepard Instruments Co., Ltd) at the certain condition for 1.5 h before testing. The proton conductivity ($\sigma$) was given out by equation (3):

$$\sigma = \frac{L}{RWd}$$  \hspace{1cm} (3)$$

where $L$ is the length of the PEM between two reference electrodes; $R$, $W$ and $d$ is the impedance, the width and the thickness of the PEM. The methanol permeability ($P$) was tested in an ATR cell (NEXUS 470, Thermo Fisher) at 40 °C with 80 v/v% methanol/H$_2$O solution as our previous report [25]. The methanol permeability could be calculated by equation (4):

$$P = \frac{4d^2D}{\pi^2}$$  \hspace{1cm} (4)$$

where $d$ is the thickness and $D$ is the diffusion coefficient. The membrane selectivity ($S$) at 40 °C of the PEMs was also calculated from the quotient of the proton conductivity measured under 100 %RH and the methanol permeability tested at 40 °C. The membrane electrode assemblies (MEAs) with active area of 4 cm$^2$ were made via hot-pressing method at 4.0 MPa for 5 min. The single cell is operated at 60 °C with 2 M methanol solution. The flux rates of methanol solution and O$_2$ are 5 and 150 mL/min, respectively.

### 3. Results and discussion

#### 3.1. Characterization of CD and NCDs

As HRTEM images shown in Fig. 1, all the NCDs are monodisperse and present near spherical morphology [19]. As shown in Fig. S1, the average diameter of CD is 5 nm while the average diameter of NCDs is ~4 nm with narrow distribution. The size of NCDs is smaller than that of CD, which might be attributed to the regulating effect of Na$^+$ on. As shown in Fig. S1, the DMF solutions of NCDs emit blue-green light excited at 365 nm UV beam, further proving the successful pyrolysis of the CA with the existence of Na$^+$. The maximum emission wavelength of NCD-0.5 is correlated to the excitation wavelength. This phenomenon is consistent with the previous report and explained by the crosslink enhanced emission (CEE) effect [21,26]. There are low lying energy sub-fluorophores in NCD-0.5 related to the heteroatom-containing bonds. Although the bandgaps of sub-fluorophores are too large for visible emission, the crosslinked structures formed during the pyrolysis process decrease the distance among heteroatom-containing groups, which strengthen the interactions among sub-fluorophores and enhance the visible emission [26]. The excitation-independent emission of NCD further verifies the influences of Na$^+$ on CA pyrolysis [18]. XPS spectra and FTIR spectra were adopted to analyze the components of NCDs. The successful modification of Na$^+$ on the carbon dots is proved by the appearance of the F 1s and S 2p peak in the XPS spectra of NCDs as well as the existence of C=O bonds attributed to Na$^+$ in high-resolution C 1s XPS spectra of NCDs (Fig. 2 and Fig. S2) [27]. The FTIR spectra also reveal the existence of multi-functional groups on NCDs, where the characteristic peaks of −COOH (3600–2500 cm$^{-1}$), −SO$_3$ (−1050 cm$^{-1}$), C=O (−1741 cm$^{-1}$), etc. could be observed (Fig. 2(c)). Besides, the slight peak shift of −SO$_3$ groups in NCDs compared with Na$^+$ demonstrates the interactions between Na$^+$ and pyrolyzed CA. Therefore, NCDs with multi-functional groups are successfully synthesized via the

![Fig. 1. TEM images of CD (a), NCD-0.3 (b), NCD-0.5 (c) and NCD-1 (d).](image-url)
pyrolysis of CA with the existence of Naflon.

The influences of the ratio between Naflon and CA on the obtained NCDs are investigated as well. The area of C 1s and S 2p peaks in the high-resolution XPS spectra of NCDs were integrated, and the peak area ratios were calculated to determine the molar ratio of C:S (Fig. 2 and Fig. S3). According to the analyses, the molar ratio of C:S, which could be used to compare the content of sulfonic groups and Naflon component in NCDs, of NCD-0.3, NCD-0.5 and NCD-1 is 18.4, 13.9 and 25.6, respectively. The content of sulfonic groups is first elevated with the increasing content of Naflon in the precursor mixture of CA and Naflon and then decreased with the excessive Naflon. According to the peak split results, C=O peak could be found in the high-resolution C1s spectrum of NCD-0.5, which demonstrates the existence of −COOH originated from citric acid in NCD-0.5 (Fig. 2 (b)). NCD-0.5 possesses the highest sulfonic group content as well as considerable oxygen-containing groups. This could be ascribed to the limited dispersibility of Naflon in the CA-based mixture due to the hydrophobic polytetrafluoroethylene backbone of Naflon. Since Naflon itself is disable to form carbon dots, Naflon becomes to agglomerate at excessive content leading to less Naflon participating in the formation of NCDs. In the high-resolution C 1s spectra of NCD-1, the lowest content of C–F bonds and the characteristic peak related to C=O bonds prove the deduction that the least Naflon participating in the formation of the composite carbon dots and the peripheral functional groups of NCD-1 mainly consists of oxygen-containing groups originated from CA [28]. Nevertheless, few C=O bond could be detected in NCD-0.3, indicating that NCD-0.3 is mostly packed with Naflon with few oxygen-containing groups from CA. Hence, the appropriate ratio between Naflon and CA in the precursor mixture plays an important role to achieve NCDs with desirable multi-functional groups.

Compared with PEI or other functionalization reagents containing amine groups, Naflon is hard to form chemical bonds with CA to develop composite carbon dots [19]. Considering the coexistence of amphipathicity of Naflon, the hydrophilicity-to-hydrophobicity transformation of CA during the pyrolysis procedure might be the motivation for Naflon's participating in the formation of NCDs, which is schematically illustrated in Fig. 3. In the beginning, CA molecules are highly hydrophilic and mainly distribute near the sulfonic groups on the side chain of Naflon to reach a balanced state. After preliminary pyrolysis, the emerging hydrophobic contents tend to distribute near the hydrophobic backbones of Naflon with the assistance of the adjustment of Naflon's backbones at the temperature above its Tg [29]. Finally, NCDs form after further pyrolysis with peripheral modification of Naflon and oxygen-containing groups. In summary, NCDs with multifunctional groups originated from Naflon (−SO3H, C–F, etc.) and CA (−COOH, C=O, −OH) are successfully synthesized via the pyrolysis of CA with the existence of Naflon. An appropriate ratio between Naflon and CA in the precursor mixture is essential to achieve the desired NCD structure. This process is probably motivated by the hydrophilicity-to-hydrophobicity transformation of CA as well as the non-covalent hydrophilic-hydrophobic interaction during the pyrolysis procedure.

### 3.2. Characterization of PEMs

Naflon contains a hydrophobic linear polytetrafluoroethylene backbone and perfluoroether side chains with extraordinarily hydrophilic sulfonic groups. The unique chemical structure bestows Naflon with a typical nanophase-separation in the membrane matrix, which develops the interpenetrating hydrophobic and hydrophilic regions during the membrane-forming process [23]. The
crystalline hydrophobic regions ensure the required mechanical and thermochemical stabilities of the membrane while the non-crystalline hydrophilic regions contain (−SO₃)n ionic clusters (5–30 nm, usually hydrated) provide the connected ionic channels for proton conduction [30]. The surface and cross-sectional morphology of the PEMs is observed with FESEM. In surface for proton conduction [30]. The surface and cross-sectional morphology of the PEMs is observed with FESEM. In surface

For the PEMs, the surface and cross-sectional FESEM images of Nafion [10] and NCD-0.5 Nafion composite PEM show the most distinct diblock morphology indicating the unique aggregation structure of ionic clusters in NCD-0.5 Nafion. As shown in the AFM image, NCD-0.5 Nafion composite PEM possesses the most connective (−SO₃)n ionic clusters (Fig. 4(d3)). Therefore, the relative lower desulfonation temperature of the NCD composite PEM demonstrates the existence of H-bonding interaction between NCD and the sulfonic groups, which slightly peak shift of −SO₃ groups (near 1049 cm⁻¹) in the FTIR spectra (Fig. 5(c)) also provide additional evidence [31]. Besides, the thermostability of the backbones of Nafion improves after the addition of NCDs. Interestingly, NCD-0.5 Nafion composite PEM shows a relatively lower desulfonation temperature and higher side chain degradation temperature among NCD Nafion composite PEMs, indicating the unique aggregation structure of ionic clusters in NCD-0.5 Nafion. As shown in the AFM image, NCD-0.5 Nafion composite PEM shows the most connective (−SO₃)n ionic clusters (Fig. 4(d3)). Therefore, the relative lower desulfonation temperature is probably caused by the stronger electrostatic repulsion among the more connective ionic clusters induced by the strong interaction between NCD-0.5 and Nafion. The adjustment of sulfonic groups consequently triggers the movement of the side chains and results in the decrease of the crystalline degree. Besides, the NCD composite membranes show restrained swelling ratio and increased elongation at break, which could be partly ascribed to the H-bonding interactions between NCDs and Nafion matrix (Figs S7 and S8). Briefly, NCDs induce the adjustment of Nafion’s aggregation structure and crystalline behavior via the hydrophilic as well as the H-bonding interaction with sulfonic groups during the membrane forming process. NCD-0.5 displays the strongest impact on Nafion among the NCDs, which is probably benefitted from the moderate hydrophilicity of NCD-0.5 and the appropriate Nafion/CA ratio of the peripheral modification layer.

As is well known, Nafion undergoes a severe dehydration at high temperature leading to a dramatic decline in the proton

Fig. 4. Cross-sectional FESEM images (a1–e1), surface FESEM images (a2 – e2) and AFM images (a3 – e3) of recast Nafion, 0.5–CD Nafion, 0.5–NCD–0.3 Nafion, 0.5–NCD–0.5 Nafion and 0.5–NCD–1 Nafion PEMs.
conductivity [32]. Interestingly, the HTWU of the composite PEMs is apparently promoted and increased with the increscent content of the oxygen-containing groups from CA in the periphery of the NCDs (Fig. 6(a)). The strong water retention ability of NCDs at high temperature could be attributed to the peripheral −COOH and −OH groups originated from CA since −COOH groups and −OH groups could form solid H-bonding interactions with water. As shown in Fig. 6, the proton conductivity of NCD Naﬁon composite is highly increased at various conditions compared with that of recast Naﬁon. 0.5-NCD-0.5 Naﬁon composite PEM shows the highest proton conductivity among the NCD PEMs. The proton conductivity of 0.5-NCD-0.5 is positively correlated with the temperature at low humidity and reaches 0.06 S cm⁻¹ at 100 °C and 40%RH, displaying a one-magnitude increase than recast Naﬁon. At 80 °C and 95 %RH, the proton conductivity of 0.5-NCD-0.5 Naﬁon (0.30 S cm⁻¹) is 5 times of the recast Naﬁon as well. Even after 12 h immersing, 0.5-NCD-0.5 Naﬁon composite PEM still possesses high proton conductivity, which further proves the good stability of the membrane.

Fig. 5. XRD patterns (a), TGA curves (b1), DTG curves (b2) and FTIR spectra (c) of recast Naﬁon, 0.5-CD Naﬁon, 0.5-NCD-0.3 Naﬁon, 0.5-NCD-0.5 Naﬁon and 0.5-NCD-1 Naﬁon PEMs.

Fig. 6. Water uptake at 30 °C in water and 100 °C–40 %RH conditions (a), temperature-dependent (40 %RH) proton conductivity (b) and humidity-dependent (80 °C) proton conductivity (c) of recast Naﬁon, 0.5-CD Naﬁon, 0.5-NCD-0.3 Naﬁon, 0.5-NCD-0.5 Naﬁon and 0.5-NCD-1 Naﬁon PEMs. XRD patterns (d), temperature-dependent (40 %RH) proton conductivity (e) and humidity-dependent (80 °C) proton conductivity (f) of 0.3-NCD-0.5 Naﬁon, 0.5-NCD-0.5 Naﬁon and 1-NCD-0.5 Naﬁon PEMs.
The significantly enhanced proton conductivity of NCD-0.5 Nafion might be ascribed to several reasons speculatively. First, the benign dispersibility of NCD-0.5 in the membrane matrix at 0.5 wt% ensures its good interaction with Nafion. Second, the good interaction between sulfonic groups and water is not influenced by the addition of NCD-0.5 since the water uptake of NCD-0.5 Nafion is close to that of recast Nafion. The third is the enhanced water retention ability at high temperature. Since water is the major carrier for proton transportation, elevated water uptake of NCD-0.5 dramatically improves the proton conductivity at harsh conditions [33]. Besides, more ionic nanochannels are constructed in the hydrophilic region in the composite PEM. On one side, more proton transportation sites are provided by the highly acidic sulfonic groups on NCD-0.5, which contributes to the high proton conductivity of Nafion under high-humidity conditions (Fig. 6(c)). Similarly, 0.5-NCD-0.3 with high –SO3H content also display high proton conductivity at 80 °C and 95 %RH on account of the sulfonic groups originated from Nafion on the periphery of NCD-0.3. Nevertheless, CD and NCD-1 present weaker effects on promoting the proton conductivity at high humidity due to the fewer sulfonic groups. On the other side, the ionic clusters become more consecutive due to the more hydrophilic region in the membrane as well as the induction of NCD-0.5 via the interaction between the multi-functional groups on NCD-0.5 and sulfonic groups in Nafion. Furthermore, the –COOH groups in NCD-0.5 might decrease the proton conduction energy barrier under low-humidity conditions [16]. This speculation is further verified by the lower proton conductivity of 0.5 NCD-0.3 than that of 0.5-CD Nafion and 0.5-NCD-1 Nafion since few –COOH groups on the periphery of NCD-0.3. In summary, NCD-0.5 with multi-functional groups displays moderate interaction with Nafion matrix and impact the aggregation structure of Nafion matrix via hydrophilic and H-bonding interaction during the membrane-forming process. The –COOH groups on NCD-0.5 largely elevate the HTWU of the composite PEM and lower the proton conduction energy barrier at low humidity while the –SO3H groups provide ideal proton transportation spots and make a great contribution to the increase in the proton conductivity at high humidity. Similarly, 0.5-NCD-0.3 Nafion and 0.5-NCD-1 Nafion also show the increased proton conductivity than that of recast Nafion under various conditions. Nevertheless, there are more or fewer disadvantages of the two composite PEMs leading to the lower proton conductivity, including the weaker activity of sulfonic groups in the membrane matrix, lower HTWU, inappropriate functional group ratio, less connected ionic nanochannels and less favored dispersibility.

The composite PEMs with different NCD-0.5 contents were prepared to testify the impact of NCD-0.5 on the proton conductivity of the membranes. NCD-0.5 Nafion composite PEMs with different nanofiller contents present superior proton conductivity to recast Nafion under various conditions, which verifies the enhancing effect of NCD-0.5 on the proton conductivity (Fig. 6(e) and (f)). As shown in Fig. S10, 0.5-NCD-0.5 Nafion displays lower desulfonation temperature, lower –SO3 FTIR peak position, higher water uptake and higher crystalline degree than those of 0.3-NCD-0.5 Nafion. This indicates the stronger interaction between NCD-0.5 and the sulfonic groups of Nafion with the increasing amount, leading to a deeper impact on the aggregation structure of the membrane matrix. Besides, more connected ionic clusters could be observed in the AFM images of Fig. S11 in consequence of the increasing NCD-0.5 content. Hence, 0.5-NCD-0.5 Nafion present the superior proton conductivity to that of 0.3-NCD-0.5 Nafion. However, slight agglomeration phenomenon appears with the excessive NCD-0.5 amount, which might be due to the excessive interfaces between NCD-0.5 and Nafion caused by the small size of NCD-0.5 (Fig. S11). The agglomeration phenomenon confines the interaction between NCD-0.5 and inevitably decreases the proton conductivity of 1-NCD-0.5 Nafion.

Methanol permeability is usually used to characterize the fuel impedance ability of the PEM for DMFC application. There is a “trade-off” effect between proton conductivity and methanol permeability due to methanol molecules and protons sharing the ionic transportation channels [34]. Despite the highly increased proton conductivity, NCD Nafion composite PEMs demonstrate similar methanol permeability to recast Nafion with highly improved proton conductivity (Table 1). The methanol permeability of 0.5-NCD-0.5 Nafion is even 50% percent lower than that of recast Nafion at 40 °C with 80 v/v% methanol concentration. On one side, the modification of Nafion’s perfluoro backbones on the periphery endows NCDs with the methanol resistance ability. On the other side, the adjustment of the aggregation structure of the membrane makes the methanol permeation channels more tortuous. Hence, the selectivity of NCD composite PEMs is substantially higher than that of recast Nafion and Nafion 117/0.5-NCD-0.5 Nafion (1.8E+06 S cm−2) shows a twenty times promotion in selectivity than recast Nafion (9.1E+04 S cm−2) at 40 °C. Besides,

**Table 1** Transport properties of the PEMs at 40 °C.

<table>
<thead>
<tr>
<th></th>
<th>Proton Conductivity (S cm⁻¹)</th>
<th>Methanol Permeability (cm² s⁻¹)</th>
<th>Selectivity (S s cm⁻³)</th>
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<tr>
<td>Nafion 117</td>
<td>4.8E-03</td>
<td>5.5E-07</td>
<td>8.7 E+03</td>
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<tr>
<td>Recast Nafion</td>
<td>1.9E-04</td>
<td>1.8E-08</td>
<td>1.1E+04</td>
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<td>2.9E+04</td>
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Fig. 7. Single DMFC performances of recast Nafion and 0.5-NCD-0.5 Nafion PEMs with 2 M methanol solution at 60 °C.
0.5-NCD-0.5 Nafion composite PEM keeps low methanol permeability and high selectivity after 12-h methanol immersing benefiting from the good membrane stability (Table S2). Therefore, high-performance NCD Nafion composite PEMs are successfully achieved, and NCDs with multi-functional groups are proved to be an effective nanofiller to promote the overall performance of the composite PEMs. 0.5-NCD-0.5 Nafion demonstrates impressive performance compared with the previous report as well (Table S2). Fig. 7 shows the single cell performance test results. The open-cell voltage of the cell with 0.5-NCD-0.5 Nafion (0.69 V) is higher than that of the cell with recast Nafion (0.62 V), which proves the lower methanol permeability in the composite PEM. The peak power density of the cell with 0.5-NCD-0.5 Nafion is 83% higher than that of the cell with recast Nafion. Besides, the maximum current density of 0.5-NCD-0.5 Nafion is 26% higher than that of recast Nafion. These testing results prove the higher through-plane proton conductivity as well as the good performance of 0.5-NCD-0.5 Nafion composite PEM, which demonstrates the great application potential in DMFC.

4. Conclusions

NCDs with multi-functional groups were successfully synthesized via the pyrolysis of CA with the existence of Nafion, which is motivated by the hydrophilicity-to-hydrophobicity transformation of CA as well as the non-covalent hydrophilic-hydrophobic interaction during the pyrolysis procedure. The appropriate ratio between Nafion and CA in the precursor mixture plays an important role to achieve NCDs with multi-functional groups. Then the NCDs were blended with Nafion to prepare NCD Nafion composite PEMs by solution casting method. Multi-functionalized NCDs display moderate interaction with Nafion matrix and impact the aggregation structure of Nafion matrix via hydrophilic and H-bonding interaction during the membrane-forming process. NCDs are proved to be an effective nanofiller to promote the overall performance of the composite PEMs. The oxygen-containing functional groups (−COOH and −OH) of NCDs substantially elevate the HTWU of the composite PEM and lower the proton conduction energy barrier at low humidity while the −SO3H groups provide ideal proton transportation spots and make a great contribution to the increase in the proton conductivity under high humidity conditions. NCD Nafion composite PEMs present a significant increase in proton conductivity under various conditions. The proton conductivity of 0.5-NCD-0.5 reaches 0.065 S cm⁻¹ at 100 °C and 40 %RH, displaying a one-magnitude increase than recast Nafion. At 80 °C and 95 %RH, the proton conductivity of 0.5-NCD-0.5 Nafion (0.305 S cm⁻¹) is 5 times of the recast Nafion as well. NCDs could also suppress the methanol crossover of the composite PEMs. The methanol permeability of 0.5-NCD-0.5 Nafion is 50% percent lower than that of recast Nafion at 40 °C with 80 v/v% methanol concentration. Therefore, high-performance NCD Nafion composite PEMs with high selectivity are successfully achieved and adaptable for high-temperature operation.

Acknowledgements

The authors are very grateful the financial support from the Ministry of Science & Technology of China (No. 2016YFA020302) as well as the DMFC test support from Professor Jiang’s group of Tianjin University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2017.11.047.

References


