Short communication

Chitosan–phosphotungstic acid complex as membranes for low temperature H$_2$–O$_2$ fuel cell

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HIGHLIGHTS

- Freestanding chitosan/H$_3$PW$_{12}$O$_{40}$ membranes were made by in situ ionotropic gelation.
- Open circuit potential was up to 0.95 V using such membranes in H$_2$–O$_2$ PEMFC at 25 °C.
- A maximum power density of 350 mW cm^{-2} was obtained at 25 °C.
- The conductivity of the membrane was up to 18 mS cm^{-1}.

ARTICLE INFO

ABSTRACT

Free-standing Chitosan/phosphotungstic acid polyelectrolyte membranes were prepared by an easy and fast in-situ ionotropic gelation process performed at room temperature. Scanning electron microscopy was employed to study their morphological features and their thickness as a function of the chitosan concentration. The membrane was tested as proton conductor in low temperature H$_2$–O$_2$ fuel cell allowing to get peak power densities up to 350 mW cm^{-2}. Electrochemical impedance measurements allowed to estimate a polyelectrolyte conductivity of 18 mS cm^{-1}.

1. Introduction

Chitosan (CS) is the N-deacetylated derivative of chitin, which is a cationic linear polysaccharide usually obtained by alkaline deacetylation of crustacean chitin and represents the second most abundant natural polymer. Due to its excellent properties, such as biocompatibility, biodegradability, non-toxicity, low-cost chitosan has found many applications in industrial areas. As cationic polyelectrolyte, CS can react with various natural and synthetic anionic species or anionic polyelectrolytes to form polyelectrolyte complexes (PECs). These complexes are generally water insoluble and make hydrogel. The gelation process is mainly related to the formation of ionic interactions between the cationic chitosan and negatively charged polyanion counterparts [1–3].

Heteropolyacids (HPAs) are strong Bronsted acid as well as solid electrolytes [4] and are considered promising materials in the fabrication of organic–inorganic nanocomposite membranes for fuel cell thanks to their high proton conductivity [5–8]. The major problems in using HPAs in fuel cell are their solubility in water and low mechanical strength, which might result in decline in cell performance with time [9–13]. To overcome this problem, it has been proposed to prepare CS and HPAs polyelectrolyte films to be employed as proton exchange membrane in low temperature fuel cell, since such PECs are reported to be insoluble [4]. A survey of the already published works showed that CS based PECs produced have been tested in direct methanol [5–8,14,15], in borohydride [16] and hydrogen [17] fed fuel cells. In the last case very poor performances were obtained due to a very low proton conductivity of the membrane.

In this paper we propose a novel procedure to fabricate homogeneous CS-HPA polyelectrolyte films using phosphotungstate acid

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(PTA) as cross-linking agent. In order to prepare flat and homogeneous membrane of controlled thickness, a porous mean, i.e. anodic alumina membrane (AAM), was firstly impregnated by PTA and then immersed in a CS containing aqueous solution to release the acid and induce the in situ gelation of chitosan [18,19]. The reaction between CS chains and PTA retained by the pores allows fabrication PEC thin films on AAM surface, that can be easily peeled off from the support, cut to any size and shape. The obtained membranes were tested in a H_2/O_2 fuel cell working at low temperature (25 °C), low humidity (T_{gas} = 25 °C) and Pt loading of 1 mg cm^{-2}. Impedance Spectroscopy was used to get information of the conductivity of the membrane as well as to model the overall electrical behaviour of the cell.

2. Experimental

Chitosan/PTA films were grown through ionotropic gelation by using commercial AAM (Anodisc-47 Whatman, pore diameters 200 nm, porosity 43% and thickness 50 μm) as support. Chitosan powder, acetic acid and $H_3PW_{12}O_{40} \times H_2O$ were supplied by Sigma–Aldrich.

CS powder (1, 2 and 3% w/v), acetic acid (2% w/v) and distilled water were mixed to achieve CS protonation and thus, solubilization. Solutions were stirred for 24 h before use and then put in contact for 30 s with PTA impregnated AAM, as depicted in Fig. 1a, in order to induce cross-linking reaction and, thus, chitosan membrane formation (see Fig. 1b and c).

Scanning Electron Microscopy analysis was performed by using a Philips XL30 ESEM coupled with EDX equipment.

The composite membranes prepared were sandwiched between two carbon paper electrodes (Toray 40% wet Proofed-E-Tek), covered with a mixture Pt black/C black (30% Pt on Vulcan XC-72, E-Tek) stirred in n-butyl acetate for at least 3 h. The catalyst loading was 1 mg cm^{-2} of platinum. The active area (2 cm^2) was delimited by insulating silicon rubber. The Membrane Electrode Assembly (MEA) was then assembled in a single fuel cell apparatus (Fuel Cell Technologies, Inc.) and fed with dry oxygen (99.5% purity, 1 bar), and hydrogen (99.5% purity, 1 bar) humidified at room temperature. Polarization curves were obtained by using a h-tec Fuel Cell Monitor (item 1950). The current density reported in the following are referred to the apparent area (2 cm^2).

Electrochemical Impedance Spectroscopy measurements were carried out through a Parstat 2263 potentiostat equipped with an Impedance Analyzer directly connected to the fuel cell. The impedance spectra were recorded in the range 10 kHz–0.1 Hz at 25 °C and open circuit potential with an ac amplitude of 10 mV. Before each measurement, the fuel cell was stabilized for at least 15 min. The Data analysis and equivalent circuit fitting were carried out through a Power Suite and a ZSimpleWin softwares.

3. Results and discussion

Chitosan solutions were prepared by dissolving CS powder in 2% w/v acetic aqueous electrolyte. CS, insoluble at neutral pH, becomes soluble at slightly acidic pH due to protonation of the NH_2 groups, according to the following reaction:

$$CS - NH_2 + CH_3COOH \rightarrow CS - NH_3^+ + CH_3COO^- \quad (1)$$

where CS-NH_2 is the chitosan under insoluble form, and CS-NH_3^+ is the protonated chitosan, soluble in water. Thus, in presence of acetic acid, the polymer behaves like a cationic polyelectrolyte, as illustrated in Fig. 1b, and can be ionically cross-linked by anionic species. Since highly concentrated PTA aqueous solution (0.38 M in this work) contains $(PW_{12}O_{40})^{3-}$ anions (lacunary or defective Keggin ions are not present, see Ref. [20]), once these two solutions are put in contact crosslinking reactions are expected to take place allowing the occurrence of in situ gelation processes. As can be appreciated in Fig. 1a if the crosslinking is pushed to take place on AAM thanks to electrolyte retained by the pores, it is possible to prepare flat and freestanding thin CS-PTA membranes (see Fig. 1c). The polyelectrolyte complexes gel is formed by cross-link of CS chains through the interaction of cationic amino groups of CS and Keggin anions (polyphosphotungstate) according to:

$$(PW_{12}O_{40})^{3-} + 3\left(CS - NH_3^+\right) \rightarrow (PW_{12}O_{40})^{3-}\left[CS - NH_3^+\right]_3$$
$$(2)$$
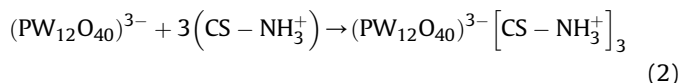
In order to favour the interactions between PTA^{3-} and NH_3^+ groups, once formed films were kept immersed in 0.38 M PTA solution for 24 h (functionalization). The morphologies of polyelectrolyte CS/PTA membranes were investigated by scanning
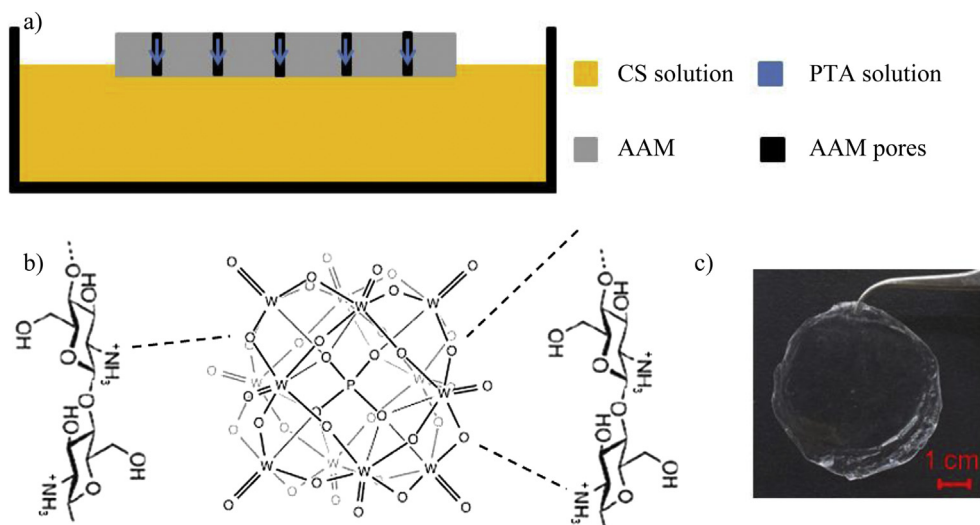

Fig. 1. a) Scheme of the contact between CS solution and PTA through the AAM pores, b) cross-linking of the CS thanks to the anionic specie PTA^{3-}, c) picture of the membrane soon after fabrication.

electron microscopy. In Fig. 2a—d we report the SEM images of CS/PTA films cross-section as a function of the chitosan concentration. The figures show that the CS/PTA membranes are homogeneous without the formation of micro-voids, typically observed in polymer film prepared through wet phase separation mechanisms [21,22]. At higher magnification (see Fig. 2b), it is possible to see that the membranes show a low porosity, as necessary to limit the gases crossover. This can be attributed to a uniform distribution of cross-links, due to the homogeneous gelation process occurring at low concentration chitosan solutions, with a close and direct contact between polymer chains and PTA^{3-} anions gelling agent, as depicted in Fig. 1a. The SEM investigation allows to conclude that the membranes' thickness was very uniform even for large area

(~17 cm^2) membranes. According to EDX analysis W and P are present all over the membrane (see Fig. 2e). As shown in Fig. 2f the membrane thickness increases by increasing chitosan concentration in the fabrication solution. Each point of Fig. 2f has been estimated averaging the thickness measured in five different areas of at least three different membranes prepared in the same experimental conditions.

In Fig. 3 we report the cell potential and the power density vs current density curves recorded with different CS-PTA membranes prepared from 1%, 2% and 3% Chitosan solutions after 24 h of functionalization. The open circuit potential (OCP) increases by increasing the CS content in the solution, thus suggesting that gases cross over becomes less significant. This is in agreement with the
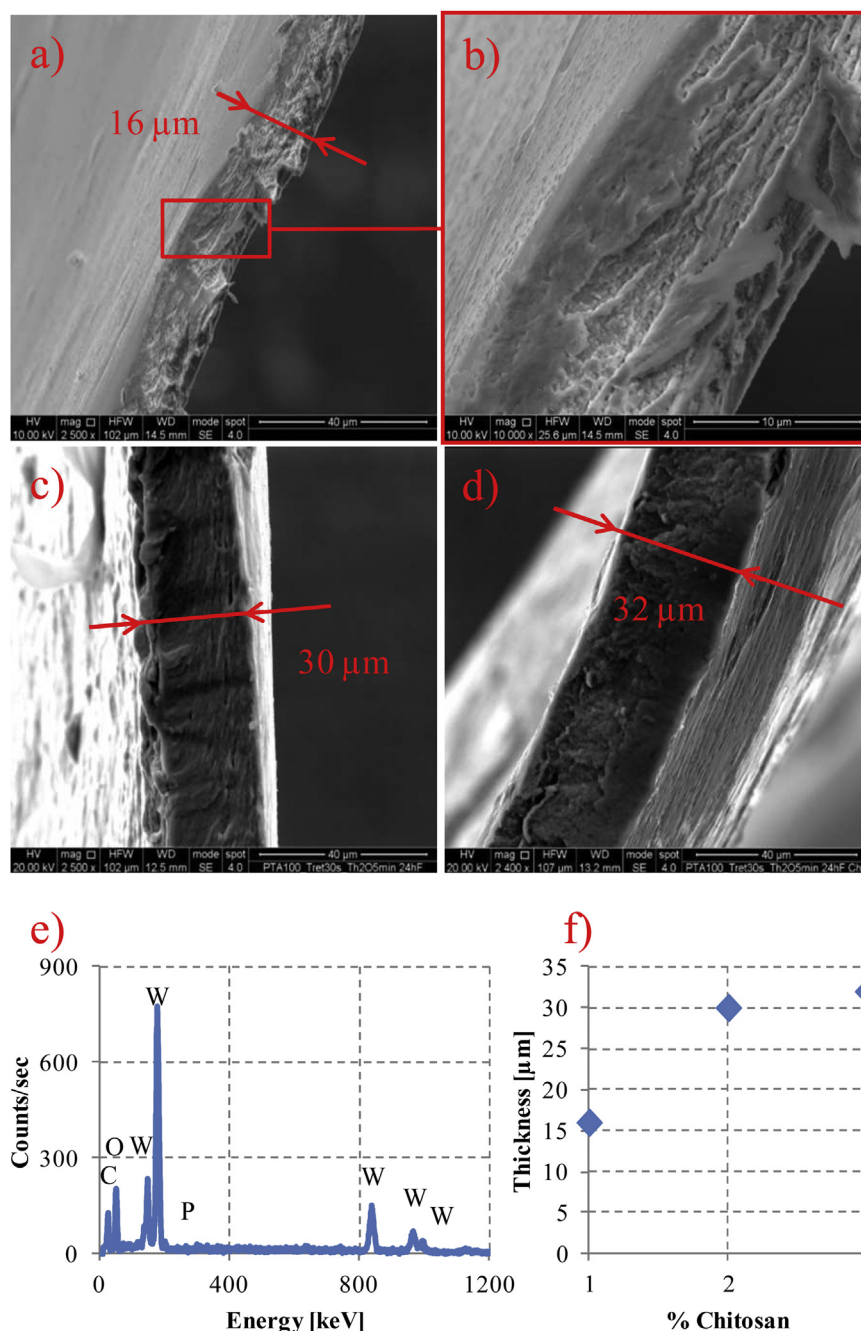

Fig. 2. SEM cross-section images of CS/PTA membranes obtained with a) and b) 1%, c) 2% and d) 3% [w/v] CS in acetic acid solution, e) EDX spectrum, f) thickness vs CS concentration estimated by SEM micrographs.
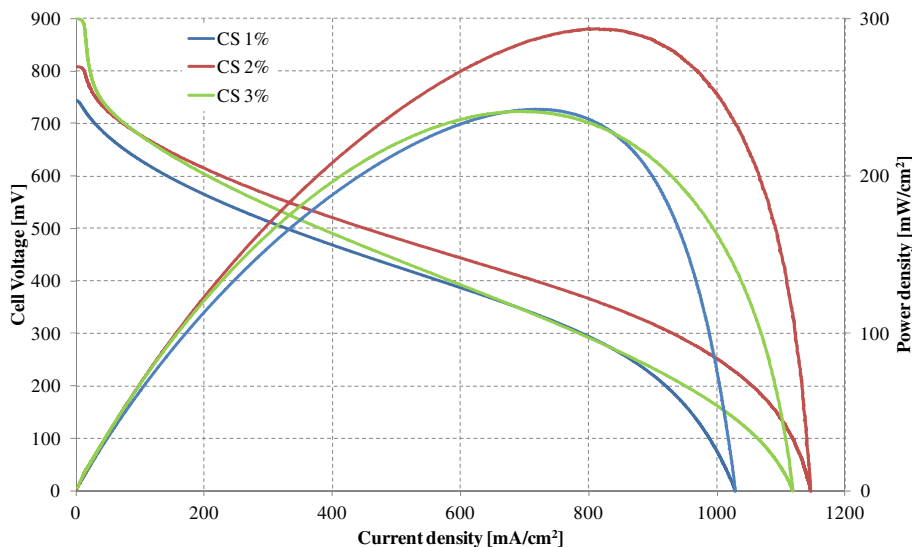
Fig. 3. Cell potential and the power density vs current density curves relating to a MEA prepared using a 1%, 2% and 3% after 24 h of functionalization carried out in the fuel cell fed with H_2/O_2 at 1 bar and 25 °C.

increasing thickness revealed by SEM micrographs on going from 1% to 2 and 3%. However, the almost comparable thickness of the membrane prepared using 2% and 3% CS solutions suggests that a more compact membrane can prepared starting from the higher concentrated solution. As shown in Fig. 3, the highest power peaks are obtained with the membranes prepared from 2% CS solution. The power peak density (~295 mW cm^{-2}) is sensitively higher with respect to values obtained by supporting phosphotungstic acid directly in the pores of AAMs [13] and higher with respect to H_2 fed fuel cell using Chitosan–PTA composite membranes prepared by solution cast process [17]. A slight increase in the gas pressure ($P_{H_2} = P_{O_2} = 1.2$ bar) and in Pt load at the cathode side (1.5 mg cm^{-2}) allowed to obtain even better performance as shown in Fig. 4 for a MEA prepared using a chitosan membrane with 2% w/v CS solution. In this polarization curve the activation region ends usually at ~750 mV (i.e. 80 mA cm^{-2}) and is followed by the occurrence of an ohmic control due to proton transport inside the membrane. Assuming as negligible the overvoltage for the H_2 oxidation, it is possible to estimate the kinetic parameters for O_2 reduction in the activation region from the Tafel plot (see inset). An apparent exchange current density, i$_0$, of $2.7 \cdot 10^{-4}$ A cm^{-2} which is in agreement with the values reported in the literature [[23] and refs. therein] and a slope of ~66 mV per current decade.

From the slope of the linear part of the polarization curve it is possible to estimate a membrane resistance of ~0.37 Ω cm^2, giving a conductivity, σ, for the CS/PTA membrane of ~8 mS cm^{-1} according to the following relationship:

$$\sigma = \frac{L}{R_m A}$$

where L is the membrane thickness (i.e. 30 μm) and A the geometric area of the membrane. This value has been compared to that estimated fitting the electrochemical impedance spectra recorded in H_2/O_2 fed fuel cell at 25 °C (gas and cell temperature) at the open circuit potential. The Cole–Cole plot for a MEA prepared using a CS/PTA membrane of 30 μm after 24 h of functionalization is reported in Fig. 5, and has been interpreted according to the equivalent circuit shown in the inset, where the parallel between R_C and C_C accounts for the charge transfer resistance and double layer capacitance at the cathode, R_{el} is representative of the membrane

ionic resistance, and the Randles circuit with Warburg element has been introduced to model the electrochemical behaviour of the anode. The R_C value estimated according to the best fitting procedure (see Fig. 5) is close to the value of charge transfer resistance, R_{ct}, predicted by the Butler–Volmer equation [24]:

$$R_{ct} = \frac{RT}{nFi_0}$$

where T is the temperature, F the Faraday constant and n (molar amount of electrons transferred per mole of reaction during rate-determining step) is 2 [23]. The contribution to the overall cell impedance arising from the H_2 electrode is usually negligible, since a very low charge transfer resistance is expected for hydrogen oxidation due to the very high catalytic activity of Pt toward such reaction. However, a diffusion control can become significant when water carried by the humidified gas and produced as a consequence of O_2 cross over can begin to saturate the tortuous pathways of the porous network [25]. This hypothesis is supported by the very low charge transfer resistance (R_A) estimated by the best fitting procedure [26], almost negligible with respect to the impedance of the Warburg element. It is noteworthy that R_{el}, which has been attributed mainly to the membrane, is lower with respect to that estimated by the slope of the polarization curve (see Fig 4), allowing to estimate a conductivity of 18 mS cm^{-1}.

4. Conclusions

Chitosan–phosphotungstic acid polyelectrolytes were prepared using anodic alumina membrane as porous medium to liberate the oxo-metallate anions and to induce the CS chains crosslinking.

After immersion for 24 h in highly concentrated phosphotungstic aqueous solutions, the prepared films were used as membrane in low temperature (25 °C) H_2–O_2 fuel cells. A significant peak power of 350 mW cm^{-2} was obtained. Analysis of the polarization curves allows to evidence the presence of a wide range of current density where the main losses arise from the membrane resistance. According to the fitting of the EIS spectra recorded at the open circuit potential, the conductivity of the membrane is ~18 mS cm^{-1}, which is slightly higher with respect to that estimated from the slope of the linear region of polarization curves.
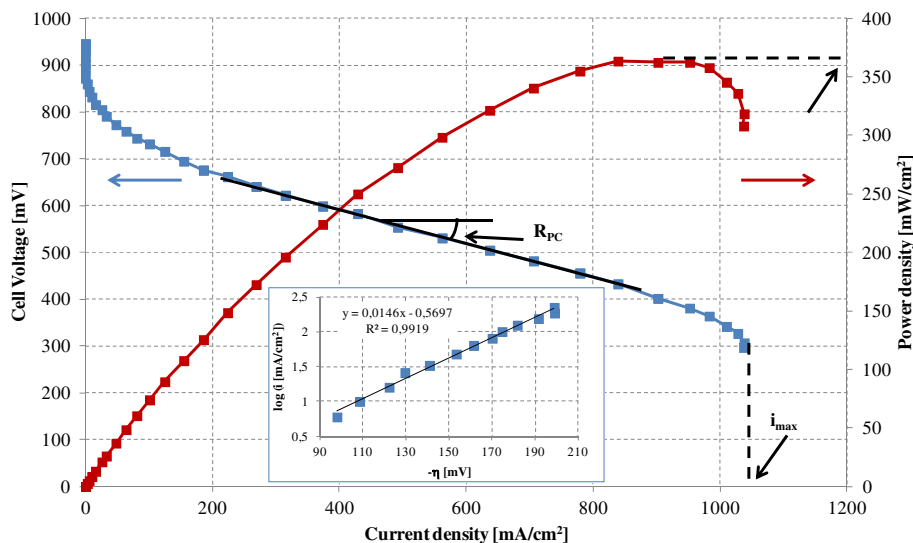
Fig. 4. Cell potential and the power density vs current density curves relating to a MEA prepared using a 2% w/v CS solution after 24 h of functionalization carried out in the fuel cell fed with H_2/O_2 at 1 bar and 25 °C. Inset: Tafel plot with $\eta = (V\text{-}iR) - OCP$.
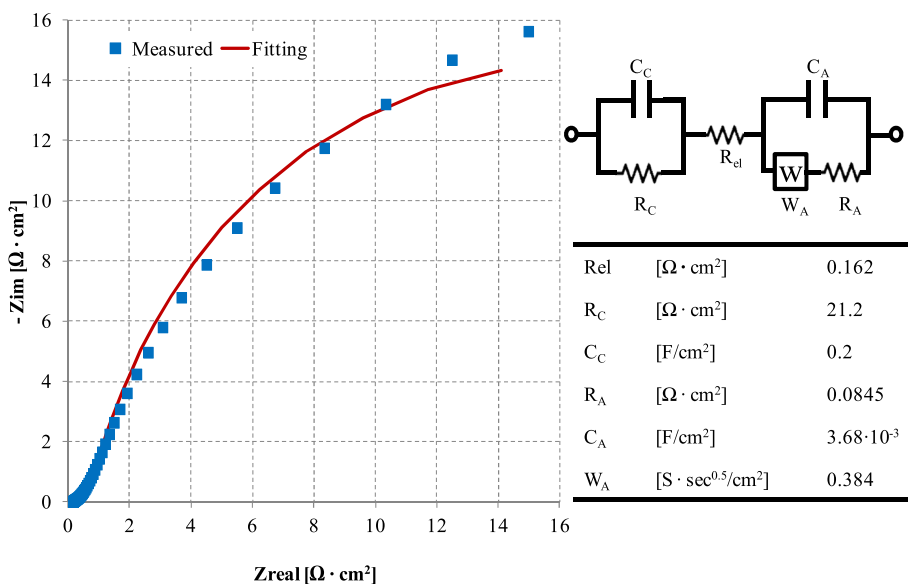

Rel	[$\Omega \cdot cm^2$]	0.162
R_C	[$\Omega \cdot cm^2$]	21.2
C_C	[F/cm^2]	0.2
R_A	[$\Omega \cdot cm^2$]	0.0845
C_A	[F/cm^2]	$3.68 \cdot 10^{-3}$
W_A	[$S \cdot sec^{0.5}/cm^2$]	0.384

Fig. 5. Cole–Cole plot relating to MEA of Fig. 4, recorded at the OCP (0.945 V).

Acknowledgements

References

[1] Y. Wan, K.A.M. Creber, B. Peppley, V. Tam Bui, J. Membr. Sci. 280 (2006) 666–674.
[2] M. Rinaudo, Prog. Polym. Sci. 31 (2006) 603–632.
[3] M. Dash, F. Chiellini, R.M. Ottenbrite, E. Chiellini, Prog. Polym. Sci. 36 (2011) 981–1014.
[4] J. Ma, Y. Sahai, Carbohydr. Polym. 92 (2013) 955–975.
[5] C. Zhao, H. Lin, Z. Cui, X. Li, H. Na, W. Xing, J. Power Sources 194 (2009) 168–174.
[6] Z. Cui, W. Xing, C. Liu, J. Liao, H. Zhang, J. Power Sources 188 (2009) 24–29.
[7] S. Mohanapriya, S.D. Bhat, A.K. Sahu, S. Pitchumani, P. Sridhar, A.K. Shukla, Energy Environ. Sci. 2 (2009) 1210–1216.
[8] S.E. Shakeri, S.R. Ghaffarian, M. Tohidian, G. Bahlakeh, S. Taranejoo, J. Macromol. Sci. 52 (2013) 1226–1241.
[9] P. Bocchetta, F. Conciauro, F. Di Quarto, J. Solid State Electrochem. 11 (2007) 1253–1261.
[10] P. Bocchetta, R. Ferraro, F. Di Quarto, J. Power Sources 187 (2009) 49–56.
[11] J. Ma, N.A. Choudhury, Y. Sahai, R.G. Buchheit, J. Power Sources 196 (2011) 8257–8264.
[12] P. Bocchetta, F. Conciauro, M. Santamaria, F. Di Quarto, Electrochim. Acta 56 (2011) 3845–3851.
[13] P. Bocchetta, F. Conciauro, M. Santamaria, F. Di Quarto, ECS Trans. 41 (2012) 79–89.
[14] Z. Cui, C. Liu, T. Lu, W. Xing, J. Power Sources 167 (2007) 94–99.
[15] M. Tohidian, S.R. Ghaffarian, S.E. Shakeri, E. Dashtimoghadam, M.M. Hasani-Sadrabadi, J. Solid State Electrochem. 17 (2013) 2123–2137.
[16] N.A. Choudhury, J. Ma, Y. Sahai, J. Power Sources 210 (2012) 358–365.
[17] S.R. Majid, A.K. Arof, Polym. Adv. Technol. 20 (2009) 524–528.
[18] Z. Jia, W. Yuan, H. Zhao, H. Hu, G.L. Baker, RSC Adv. 4 (2014) 41087–41098.
[19] H. Hu, W. Yuan, H. Zhao, G.L. Bakery, J. Polym. Sci. A Polym. Chem. 52 (2014) 121–127.
[20] Z.R. Zhu, R. Tain, C. Rhodes, Can. J. Chem. 82 (2003) 1044–1050.
[21] V. Kaiser, C. Stropnik, V. Musil, M. Brumen, Eur. Polym. J. 43 (2007) 2515–2524.
[22] Z. Yi, L. Zhu, Y. Xu, Y. Zhao, X. Ma, B. Zhu, J. Membr. Sci. 365 (2010) 25–33.

[23] J. Mainka, G. Maranzana, J. Dillet, S. Didierjean, O. Lottin, J. Power Sources 253 (2014) 381–391.

[24] Q. Guo, M. Cayetano, Y.M. Tsou, E.S. De Castro, R.E. White, J. Electrochem. Soc. 150 (2003) A1440–A1449.

[25] S. Cruz-Manzo, R. Chen, J. Electroanal. Chem. 702 (2013) 45–48.

[26] H.-Y. Tang, A.D. Santamaria, J. Bachman, J.W. Park, Appl. Energy 107 (2013) 264–270.