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Short communication

Synthesis of anion exchange membranes from cellulose: Crosslinking with diiodobutane

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ABSTRACT

Polymer Electrolyte Fuel Cells operating in alkaline media present various advantages. As an alternative to fossil origin polymer electrolytes, the synthesis of crosslinked anion exchange membranes based on cellulose is described in this paper. Using cellulose *p*-toluenesulfonate derivatives, a carbohydrate polymer bearing quaternary ammonium moieties is synthesized by a reaction with 1,4-diazabicyclo[2.2.2]octane. Membranes are then obtained by crosslinking this cationic polymer with diiodobutane. IR and NMR spectroscopy together with elemental analysis confirmed structures of the different intermediates. In order to complete this study, Ionic Exchange Capacity, Water Uptake and conductimetry data are also provided.

1. Introduction

Since the 1950s, various types of Fuel Cells have been developed as highly efficient and clean electric energy generators (Iojoiu et al., 2006; Kordesch & Simader, 1995). These power sources are usually considered for stationary applications but, more recently, compact cells have been designed, such as Proton Exchange Membrane Fuel Cells (PEMFC) which have been used to power electrically propelled vehicles.

Alkaline Fuel Cells (AFC) have an economic advantage since in an alkaline medium, electrodes can employ non-noble metal catalysts (such as silver or nickel) instead of the much more expensive metal, platinum (Gamburzev, Petrov, & Appleby, 2002). However, the use of strong alkali solutions as electrolytes presents the risk of leakage of a highly corrosive liquid and complications due to contamination by carbon dioxide. The latter can be the source of carbonate precipitation in an electrolyte which can block electrodes, with the consequence of possible flooding (McLean, Niet, Prince-Richard, & Djilali, 2002; Varcoe & Slade, 2005). Therefore using a solid, instead of a liquid polymer electrolyte lowers both risks (Agel, Bouet, & Fauvarque, 2001; Iojoiu et al., 2006; Varcoe & Slade, 2005). To-date, all protonic or anionic solid electrolytes are relatively expensive, and anionic membranes are still very fragile; hence, a cheaper and stronger polymeric structure could likely resolve these problems.

Cellulose is a very abundant natural polymer since it is readily extracted from in a variety plants (mainly wood, cotton and flax) grown in large amounts for various commercial applications. Furthermore, it is highly resistant to mechanical strain and can be easily modified to obtain films and ion exchange membranes (Yue, McEwen, & Cowie, 2002). Moreover, cellulose is stable in very concentrated basic solutions (Knill & Kennedy, 2002) which makes it an ideal raw material for conversion into anion exchange membranes. In the present work, our aim was to synthesise cellulose-based anionic membranes bearing quaternary ammonium functions.

2. Experimental

2.1. Materials

All materials were purchased from Acros, except microcrystalline cellulose and diiodobutane (Aldrich), *p*-toluenesulfonyl chloride (Alfa Aesar), diethyl ether (SDS), and ethyl acetate (Carlo Erba). All the solvents were used as received. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was stored at 4 °C.

IR spectra were performed with potassium bromide samples on a Perkin-Elmer FT-IR Spectrum 1000.

NMR spectra (^{1}H, ^{13}C and COSY ^{1}H) were obtained with a Brucker DPX 400. The acquisition frequencies used were 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C.

The elemental analyses were performed by the “Service Commun d’Analyse du CNRS” in Vernaison. The collected data were

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used to determine the different degrees of substitution (DS) and the average weight *M* of an anhydroglucose unit (AGU).

2.2. Methods

2.2.1. Dissolution of cellulose

Cellulose (20 g, 0.123 mol) was washed with methanol (3 × 100 mL) for 30 min. The same washing procedure was performed in *N*,*N*-dimethylacetamide (DMAc). The treated cellulose was then added to DMAc (1 L) containing LiCl (70 g). The mixture was stirred at 70 °C for 4 h and then overnight at room temperature.

*2.2.2. Synthesis of cellulose p-toluenesulfonate (**1**)*

The aforementioned solution of cellulose (10 g, 0.062 mol in 500 mL) was stirred with triethylamine (78.5 mL, 0.555 mol, 9 eq) at 4 °C under a flow of argon. *p*-Toluenesulfonyl chloride (64.73 g, 0.34 mol, 5.5 eq) as a powder was then added slowly to avoid a temperature rise over 8 °C. The solution was further stirred for 24 h at 4–8 °C under an argon atmosphere. The mixture was precipitated slowly by pouring into stirred iced water and strongly shaken in a flask for 15 min. The yellowish solid was removed by filtration under vacuum, and washed with ethanol (3 × 500 mL) under reflux. After removal of the ethanol by filtration under vacuum, a white solid was collected and dried under vacuum to give the product **1** (26.627 g).

IR data (cm^{-1}): 3060 (C–H arom), 2920 (C–H sp^3), 1598, 1496 and 1455 (C–C arom), 1363 and 1177 (S–O). ^1H NMR data (DMSO*d6*) δ (ppm): 7.79 ($H_{2,6}$ Ts), 7.42 ($H_{3,5}$ Ts), 5–3.5 (H cellulose backbone), 2.40 (CH_3 tosyl). ^{13}C NMR data (DMSO*d6*) δ ppm: 144.8 (C-4 Ts), 132.0 (C-1 Ts), 130.1 (C-3, 5 Ts), 127.7 (C-2, 6 Ts), 103.0 (C-1 cellulose backbone), 60.0–80.0 (C-2, 6 cellulose backbone), 21.0 (CH_3 Ts).

The average molar weight M_1 of the anhydroglucose units (AGU) of the resulting polymer **1** and the degree of substitution (DS) for tosylate and chlorodeoxycellulose (DS_{Ts} and DS_{Cl}) were obtained using the following equations.

$$M_1 = 100 \cdot \frac{6}{(\%_C/M_C) - 7(\%_S/M_S)}$$

$$DS_{Ts} = \frac{\%_S}{M_S} \cdot \frac{M_1}{100}$$

$$DS_{Cl} = \frac{\%_{Cl}}{M_{Cl}} \cdot \frac{M_1}{100}$$

*2.2.3. Synthesis of 4-aza-1-azoniabicyclo[2.2.2]octanyldeoxycellulose (**2**)*

A solution of cellulose *p*-toluenesulfonate (**1**) (10 g, 0.021 mol) and DABCO (23.87 g, 0.213 mol, 10 eq) in dimethylformamide (200 mL) was refluxed with stirring using a temperature controlled oil bath at 70 °C for 3 days. A product was precipitated by stirring in ethyl acetate (1.4 L). After decantation, the wet solid was washed with ethyl acetate (4 × 1.4 L), then with diethyl ether (5 × 1.4 L) and dried under vacuum at 40 °C over phosphorous pentoxide to give the product **2** (12.95 g).

IR data (cm^{-1}): 2962 (C–H sp^3), 1598 and 1495 (C–C arom), 1463 (C–N), 1363 and 1177 (S–O). ^1H NMR data (DMSO*d6*) δ (ppm): 7.80 ($H_{2,6}$ Ts), 7.50 ($H_{2,6}$ TsO^-), 7.43 ($H_{3,5}$ Ts), 7.12 ($H_{3,5}$ TsO^-), 4.5–3.5 (H cellulose backbone), 3.01 (H DABCO), 2.42 (CH_3 Ts), 2.29 (CH_3 TsO^-). ^{13}C NMR data (DMSO*d6*) δ (ppm): 145.1 (C-4 TsO^-), 145.0 (C-4 Ts), 138.0 (C-1 TsO^-), 129.7 (C-3, 5 Ts), 128.7 (C-3, 5 TsO^-), 127.7 (C-2, 6 Ts), 125.4 (C-2, 6 TsO^-), 60.0–100.0 (cellulose backbone), 53.0 (C_{DABCO} α N+), 44.6 (C_{DABCO} α N), 21.1 (CH_3 Ts), 20.7 (CH_3 TsO–).

The average molar weight M_2 of an AGU of the polymer **2**, the $DS_{tosylates}$ (for residual functions together with free anions) and the DS_{DABCO} were calculated using the following equations.

$$M_2 = 100 \cdot \frac{6}{(\%_C/M_C) - 7(\%_S/M_S) - 3(\%_N/M_N)}$$

$$DS_{DABCO} = \frac{\%_N}{M_N} \cdot \frac{M_2}{200}$$

$$DS_{tosylates} = \frac{\%_S}{M_S} \cdot \frac{M_2}{100}$$

*2.2.4. Crosslinking: synthesis of the anion-exchange membrane **3***

Diiodobutane (0.5–1.5 eq) was added to a solution of DABCO–cellulose (**2**) (380 mg, 0.613 mol, 0.736 mol of DABCO) in DMF (10 mL). The mixture was heated at 40 °C for 30 min and poured into an 8 cm diameter Petri dish. After 3 days, when all the solvent had evaporated, the membrane was dampened with water and easily removed from its mould.

2.2.5. IEC measurements and Water Uptake (WU)

Tosylate anions were replaced by hydroxide anions by dipping the membrane into a concentrated solution of sodium hydroxide (6 M) for 3 days. The membrane was then rinsed with distilled water, dried with paper and dipped into $V_{HCl} = 40$ mL of a hydrochloric acid solution ($C_0 = 5$ mM). After 24 h, the concentration of the solution in hydrochloric acid was determined by titration with 5 mM sodium hydroxide. The membrane was then dried under vacuum in the presence of phosphorous pentoxide and weighted.

The IEC was calculated with the equation below:

$$IEC = \frac{(C_0 - C_{+24\ h}) \cdot V_{HCl}}{m_{dry}}$$

WU was calculated by comparing the weight of a wet membrane (dried with paper) with the weight of the same membrane dried under vacuum in the presence of phosphorous pentoxide.

$$WU = \frac{m_{wet}}{m_{dry}} - 1$$

2.2.6. Conductivity measurements

In order to determine the conductivity of the membrane **3**, it was first immersed in a 1 M alkaline solution and left to equilibrate for one night, for completion of the exchange of tosylate anions by hydroxyl anions. The membrane was removed from the alkaline solution and placed between two gold coated glass plates to work as blocking electrodes. The resulting conductivity cell was connected to a frequency analyser (Autolab PGSTA30) and the impedance measured between 10 kHz and 0.1 Hz. The value of the resistance measured was obtained by extrapolation of the linear part up to the real axis, when only the electrolyte resistance remained. By measuring the membrane thickness $e_{membrane}$ and its surface *S*, the conductivity of the membrane was given by the following equation.

$$\sigma_{membrane} = \frac{1}{R_{membrane}} \cdot \frac{e_{membrane}}{S}$$

3. Results and discussion

The strategy to convert cellulose into a crosslinked anion exchange membrane that is water insoluble involved converting some of the cellulose hydroxyl groups into quaternary ammonium functionalities and using amine groups to form cross-linkages with

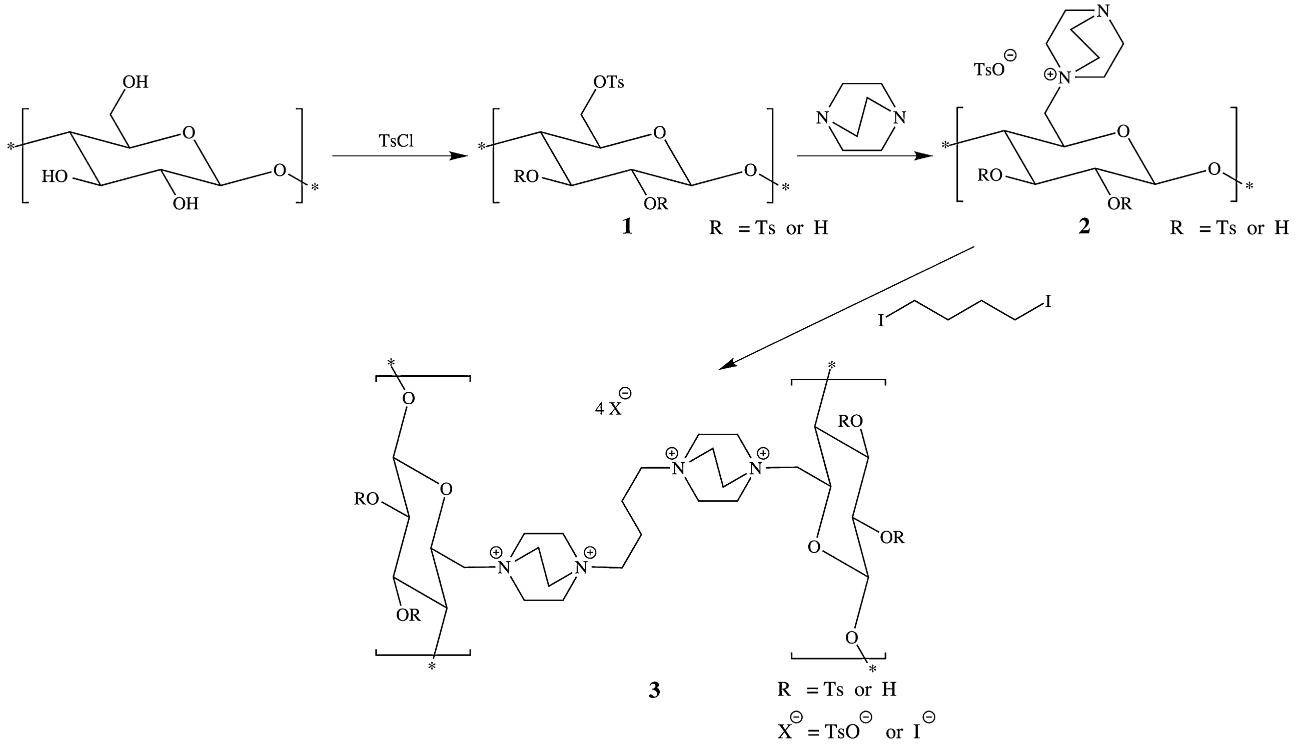

Fig. 1. Synthesis strategy of the anion-exchange membrane **3**.

a dihalogenoalkane. More specifically, the cellulose was first tosylated to give the cellulose *p*-toluenesulfonate **1**. The quaternary ammonium functional groups were introduced by reacting **1** with the tertiary diamine, 1,4-diazabicyclo[2.2.2]octane (DABCO) to give DABCO-cellulose (**2**). However, the resulting polymer **2** is slightly water-soluble, thus unsuitable for membrane preparation unless it is crosslinked. Therefore the necessary crosslinking step was undertaken by reacting **2** with diiodobutane to give **3**, as a water insoluble anion-exchange membrane (Fig. 1).

3.1. *Tosylation of cellulose*

Cellulose is difficult to dissolve due to its numerous inter- and intramolecular hydrogen bonds. However, the polar DMAc/LiCl system has been found to be an efficient cellulose solvent suitable for homogeneous reactions (Ass, Ciacco, & Frollini, 2006; Hassan, Moorefield, Kotta, & Newkome, 2005; Satgé, Granet, Verneuil, Branland, & Krausz, 2004) and the most convenient for use in the preparation of cellulose *p*-toluenesulfonate (**1**) (Heinze & Rahn, 1997; McCormick, Dawsey, & Newman, 1990; Rahn, Diamantoglou, Klemm, Berghmans, & Heinze, 1996). Therefore the reaction between cellulose and *p*-toluenesulfonyl chloride to give **1** was performed using these reagents but at low temperature (below 6 °C) to avoid the side formation of chlorodeoxycellulose, usually observed at high temperatures (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998; McCormick et al., 1990).

DS_{Ts}, DS_{Cl} and M_1 were calculated from elemental analysis of carbon, sulfur and chlorine. The results of three similar experiments are shown in Table 1 as examples.

As expected, chlorodeoxycellulose is scarcely formed as revealed by DS_{Cl} not exceeding 0.1. For this reason, DS_{Cl} is neglected and the molar weights are rounded by ten; thus, DS_{Ts} remains at 2.2 and M_1 becomes 510 g mol^{-1}.

3.2. *Quaternization of cellulose*

Quaternary ammonium sites in structure **2** are obtained by the reaction of cellulose *p*-toluenesulfonate (**1**) with DABCO in the manner reported in the literature (Abel et al., 2002; Cohen, Castro, Han, Behaj, & Engel, 2000). High values of IEC can be achieved with quaternary ammonium DABCO derivatives and the resulting cations are known to be resistant towards hydroxide anions, which makes this bulky diamine particularly suitable for this work (Agel et al., 2001; Cherestes & Engel, 1994; Iojoiu et al., 2006).

Values of DS_{DABCO} and M_2 are determined by calculation based on the elemental analysis of carbon, nitrogen and sulfur. By this method, the number of tosylate moieties is calculated per AGU ($DS_{tosylates}$), whether attached to the cellulose backbone or counter anions of the quaternary ammonium sites. The results of three similar experiments are shown in Table 2.

Even with a large excess of DABCO, the total substitution of tosylate by the tertiary amine is never achieved, since DS_{DABCO} does not exceed 1.2 units per AGU. This is probably due to the sterically hindered environment of the tosylate groups. A bulky amine like DABCO should readily reach most of the primary C–6 tosylates but a number of the secondary tosylates are much less accessible.

It can also be noticed that the values of $DS_{tosylates}$ are below 2.2. This loss of sulfur analysis can be explained by the exchange of

Table 1
Elemental analysis of cellulose *p*-toluenesulfonate (**1**).

Experiment	%C	%S	%Cl	DS_{Ts}	DS_{Cl}	M_1 (g mol^{-1})
i	49.95	13.79	0.79	2.2	0.1	523
ii	49.98	13.30	0.40	2.0	0.05	477
iii	50.05	13.77	–	2.2	–	516

Table 2
Elemental analysis of quaternary ammonium cellulose **2**.

Experiment	%C	%S	%N	DS_{DABCO}	$DS_{tosylates}$	$M_{\mathbf{2}}$ (g mol^{-1})
i	51.30	9.74	4.98	1.0	1.7	550
ii	50.00	8.22	5.83	1.1	1.4	550
iii	50.61	9.30	5.66	1.2	1.8	620

Table 3
IEC measures and Water Uptake.

Entry	eq DIB[a]	Thickness (μm)	IEC (meq g^{-1})	WU (%)	Surface (cm^2)	Resistance (Ω)	Conductivity (S cm^{-1})
a	0.5	150	3.04	250	–	–	–
b	0.5	120	3.02	252	2.9	4.2	5.4×10^{-3}
c	0.5	130	3.56	559	–	–	–
d	1.5	90	2.08	220	–	–	–
e	1.5	220	3.17	240	4.35	4.2	1.1×10^{-3}
f	1.4	90	3.43	450	1.5	26	2.5×10^{-4}
g	1.4	200	2.73	230	4.35	7.3	6.3×10^{-4}
h	1.3	80	2.43	102	1	2.3	4.3×10^{-3}
i	1.3	200	3.40	210	3.2	6.5	9.6×10^{-4}

[a] eq DIB: quantity of diiodobutane in eq per mole of DABCO.

tosylate anions with other counter ions during the reaction or the washing process. For further calculations, DS_{DABCO} is 1.2, and $M_{\mathbf{2}}$ is 620 g mol^{-1}.

3.3. *Crosslinking and casting*

Anion exchange membranes are often cross-linked to strengthen their structure. Cross-linking has already been performed on a membrane with gaseous dibromoethane; however, the system described is difficult to use and only crosslinks the surface of the membrane (Métayer & M'Bareck, 1997). Operating in homogeneous solution phase allows crosslinking throughout the whole membrane, but excessive crosslinking leads to a solid gel that is impossible to cast. Longer liquid di-halogenoalkanes are known to easily form bonds with DABCO, thus creating quaternary ammonium salts (Cohen & Engel, 1998). The use of such molecules for the crosslinking of **2** would also result in the increase of the IEC of the membrane. In this work, the polymer in solution is crosslinked by alkylation with 1,4-diiodobutane under moderate heat to allow the membranes to form with at the same time as solvent evaporation and casting take place. The membranes obtained are insoluble in all solvents, showing that crosslinking had occurred.

3.4. *Characterization of the membranes **3***

Ionic Exchange Capacity (IEC), Water Uptake (WU, weight increase by humidification of a dry membrane) and conductivity were measured for the membranes obtained and are presented in Table 3. The values of IEC obtained for membranes **3** are in the range 2–3.5 meq/g, which are above 1 meq/g that is the range of classical membranes for fuel cell use. Experiments a, b and c show (Table 1) that for the same preparation of membrane **3**, the IEC could vary according to thickness. High WU values were obtained for each membrane reflecting a high affinity for water which is most likely to be due to the presence of the numerous cationic sites. The membranes were found to be fragile which may be due to the membrane have a gel-like structure with a low crosslinking ratio of the cellulosic chains. Finally, conductivity measurements were found to be in the range between 2×10^{-4} and 5×10^{-3} S cm^{-1} which are somewhat difficult to link with the operating conditions of the crosslinking reaction. Conductivity depends on numerous parameters, and some of them (such as relative humidity of the membrane) can be difficult to monitor. Nevertheless, the conductivities obtained in this preliminary study are promising, as they better reach roughly the same values as the well recognised anion exchange membranes previously cited in this report (Agel et al., 2001).

4. Conclusion

This work shows the successful and facile preparation of anionic membranes from cellulose as an inexpensive and renewable starting material. The membranes produced show high concentrations of cationic sites together with promising conductivity values. These properties point to future generations of such types of carbohydrate membranes derived from cellulose having potential electrochemical applications. The weakness observed could be overcome by improving the reticulation rate, leading to more highly crosslinked membranes having increased the IEC values.

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