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Sodium polymer electrolytes composed of sulfonated polysulfone and macromolecular/molecular solvents for Na-batteries

C.S. Martinez-Cisneros^{1*}, C. Antonelli², B. Levenfeld¹, A. Varez¹, J.Y. Sanchez^{1,3*}

¹ Materials Science and Engineering Department, University Carlos III of Madrid, Spain.

² Univ. de Montpellier, Institut Européen des Membranes, UMR 5635, CNRS, ENSCM, Place Eugene Bataillon, F-34095 Montpellier, France.

³ UJF UdS, Grenoble INP, LEPMI, UMRCNRS5279, 1130 Rue Piscine, BP75, F-38402

S^t Martin d'Hères, France.

*corresponding authors: cymartin@ing.uc3m.es; jeasanch@ing.uc3m.es

Abstract

Polysulfone acidic ionomers have been extensively used as Fuel Cell membranes, mainly because of their mechanical, thermal, chemical and electrochemical stability as well as their excellent film-forming capability. This contribution deals with the development of blends based on polysulfone-sodium sulfonate and macromolecular/molecular solvents, consisting of poly(oxyethylene), POE, and propylene carbonate, PC, respectively. The objectives were to take advantage both of the thermomechanical performances and of the macromolecular polyanions provided by the polysulfone ionomer. Combining POE/PC solvents, didn't allow obtaining sufficient

blend's conductivities. On the other hand, addition of very low amounts of sodium perchlorate led to appreciable conductivities.

Keywords: sodium battery; polymer electrolyte, Sodium perchlorate; polyethylene oxide, sulfonated polysulfone.

1. Introduction

Motivated by the expected growth of smart grid's needs in inexpensive and sustainable energy storage, alternatives to lithium batteries have lately aroused a great research interest [1,2]. In this sense, other alkaline (Na) and alkaline-earth (Mg, Ca) elements have been proposed as promising substitutes of lithium. This mainly responds to their low reduction potential, high availability, significant capacity and low price. Research in magnesium batteries has been lately intensified [3] since 2007 [4], including some blends of δMgCl_2 and Ionic Liquids, which allow a Mg anode to be cycled [5].

Regarding calcium batteries, although Ca^{2+} has been successfully intercalated in crystallized and amorphous V_2O_5 with high initial discharge capacities (450 and 560 mAh/g, respectively) [6,7], probably associated to the lack of performing electrolytes, they have not received enough attention [8].

On the other hand, among the electrochemical couples, the Na/Na⁺ one has received more attention as sodium batteries are already commercialized and are expected to be significantly cheaper than lithium-ion ones [9,10]. Nowadays, most researches focus on new anodes and cathodes and not enough attention is paid to the non-electroactive materials, i.e. separators and electrolytes, whose contributions have a significant impact not only on the overall battery cost but also on its safety, making their improvement essential. The electrolytes can be roughly ranked into solvent-free electrolytes and

solvent-based electrolytes. The formers are either inorganic solids as NASICON® or β -Alumina, both providing high safety and single-cation transport but facing issues to be shaped into thin membranes, or solvent-free polymer electrolytes that can reach acceptable conductivities at high temperature [11–14]. On the other hand, solvent-based electrolytes, which either consist of organic aprotic solvents, Ionic Liquids [15] or their mixtures, require to be trapped into dense membranes or in macroporous separators. Ionic liquids present low flammability and thermal, chemical and electrochemical stability. However, their high cost and increase in viscosity when salts required for ionic conduction are added [16], leading to lower ionic mobility, has limited their application in batteries. Some studies report the immobilization of ionic liquids in polymer electrolytes in order to improve their ion transport properties without a severe loss in mechanical properties [17].

When liquid electrolytes are required, commercial macroporous separators, e.g. Celgard® or Solupors®, exhibit significant advantages as high mechanical strength up to their fusion, possible shut-down (tri-layered Celgard®) but also severe drawbacks as high ohmic losses, highlighted by McMullin Numbers ranging between 5 and 18 [18–21], and pore's clogging upon heating [22]. Alternatively, dense polymeric films can be swelled by liquid electrolytes that, since the first report by Feuillade et al.[23], were named plasticized, gelled or hybrid polymer electrolytes. This contribution deals with blends and semi-interpenetrated networks (semi-IPN) made of a Na-conducting ionomer and a solvating polyether. Commercial PFSA (perfluorosulfonic acid) ionomers exhibit, as Fuel Cell membranes, outstanding proton-conductivities. Their Ionic Exchange Capacity (IEC), which barely reaches 0.9 meq/g, is well-adapted for use as PEMFC membranes, but insufficient for the targeted blends and semi-IPN. Additionally, PFSA based ionomers are very costly. Therefore, in this work, we propose the use of a Na

ionomer based on a high performance polymer backbone, whose aryl repeat units allow IEC to be easily modulated through electrophilic substitution. Among modifiable High Performance polymers it can be quoted, polysulfone (PSU), polysulfide (PSF), polyether-ether-ketone (PEEK) and polyphenylene oxide (PPO). Despite their high crystallinity, which hinders their modification, PEEK and PSF can be sulfonated. However, both were discarded as they evidenced, from a comparative electrochemical study [24], instability either in reduction (PEEK) or in oxidation (PSF). Regarding PPO, the commercial samples have, contrary to the High Performance polymers prepared by polycondensation, a broad Molecular Weight Distribution (MWD) with significant amounts of oligomers. On the other hand, PSU and its sulfonated form were found to exhibit the broadest electrochemical stability window of the High Performance polymers and ionomers [24]. Additionally, it can be sulfonated, using a fairly mild sulfonating reagent, trimethylsilyl-chlorosulfonate (TMSCS), which allows the reaction to proceed in homogeneous conditions [25,26]. Furthermore, chain breakings that may occur during PSU sulfonation, leading to brittle films, can be avoided by using an argon stream that removes the HCl by-product [27]. Hence, the ionomer PolySulfone Sodium Sulfonate (SPSU-Na) was chosen for this study. Additionally, it must be emphasized that SPSU-Na is the direct product of PSU sulfonation by TMSCS, obtained by the precipitation of the reaction medium in EtONa/EtOH. Being therefore the precursor of acidic ionomers used in PEFC membranes, it should allow polymer electrolyte cost-cutting. SPSU-Na was first blended with commercial linear POE and networks based on comb POE, to assess the ionic conduction performances in liquid solvent-free configuration. Thereafter the blends were swelled with the high boiling point solvent PC. Last, NaClO₄ was added, at very low concentration, in order to minimize safety issues, while benefiting of a Na⁺ reservoir provided by the Na-rich SPSU-Na.

2. Experimental

2.1. Materials and Polymer blend preparation

All reagents were supplied by Sigma-Aldrich in analytical grade. Sulfonated polysulfone in the sodium salt form (SPSU-Na) was synthesized according to a method previously reported [26]. The sulfonation degree, determined by ^1H NMR spectroscopy, was 2.5 meq/g.

As a first approach, polymer electrolytes were prepared at different O/Na ratios (8, 12, 16, 20 and 25) by a combination of lyophilization and hot-pressing [14] dissolving SPSU-Na and poly(oxyethylene) (POE) (M_w 3×10^5 g/mole) in deionized water by stirring during six hours at 40°C . The obtained solutions were then frozen at -30°C and later lyophilized (FreeZone¹, LABCONCO, USA) during 48 hours. The material so obtained was hot pressed between two stainless steel plates ($100 \times 100 \times 5 \text{ mm}^3$) by applying pressure and temperature (50 kN ; 100°C). The films so obtained were homogeneous, mechanical stable and had a thickness ranging from $75 \mu\text{m}$ to $100 \mu\text{m}$.

For the second approach, specific amounts of SPSU-Na, poly(ethylene glycol) dimethacrylate (DI-PEGMA; average $M_n \sim 550$) and poly(ethylene glycol) methyl ether methacrylate (MONO-PEGMA; average $M_n \sim 500$) were dissolved in N, N-Dimethylacetamide (DMAc) by stirring during 4 hours. Once the mixture appeared to be homogeneous, 2 wt% benzoyl peroxide was added as initiator and dissolved by stirring. Solutions were degassed to remove air bubbles and later poured onto glass petri dishes. The solvent was evaporated in an oven using a previously optimized thermal cycle: (1) 80°C for 24h, (2) 110°C for 2h and (3) 130°C for 2h. The material so obtained was washed in abundant acetone, dried at 50°C under vacuum and later hot-pressed (120°C ; 20 kN). Using this methodology, films with thickness ranging from $120 \mu\text{m}$ to $165 \mu\text{m}$ were obtained.

To remove any residual traces of solvents, blend membranes obtained by both approaches were, previous to any characterization or measurement, dried under vacuum at 50°C during 12 hours to prevent the adsorption of water. Afterwards, samples were stored in a glove box (M. Braun, GmbH, Germany) filled with argon, in which moisture was lower than 1 ppm. In both cases, to improve ionic conductivity, propylene carbonate (PC) was included in the polymer network by swelling membranes in it.

2.2. X-Ray diffraction

X-Ray diffraction (XRD) measurements were carried out using a Philips X'PERT MPD diffractometer (Cu K α radiation) operating at 40 kV and 40 mA. This instrument has ($\theta/2\theta$) Bragg–Brentano geometry and it is equipped with a curved graphite monochromator. Data were taken with a 0.5° divergence slit, a receiving slit of 0.01° and a set of Soller slits with axial divergence of 1°. The XRD patterns were recorded over a 2θ range of 5–80° using a step scan of 0.02° and a counting time of 1 sec per step. During recording, samples (thin films) were placed onto a zero-background Silicon holder.

2.3. Thermal and thermomechanical analyses

The thermogravimetric analysis (TGA) of ~9 mg samples was performed using a Pyris TGA (Perkin Elmer, USA) thermogravimetric analyzer. Samples were heated in a platinum crucible from 30°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere. Onset temperature (T_{onset}) was determined as the point of intersection of the tangent drawn at the point of greatest slope with the extrapolated base line. For differential scanning calorimetry (DSC) studies, we used a DSC822e (Mettler Toledo, Switzerland) under a 50 mL/min constant N $_2$ (g) flow on ~7 mg samples. Samples were

heated from 30°C to 150°C (10°C/min), then cooled down (-20°C/min) and heated up from -100°C to 250°C (10°C/min).

The mechanical properties of the polymer electrolytes were studied by Dynamic Mechanical Thermal Analyses (DMTA) using a DMA Q800 (TA Instruments, USA) working in tensile mode at 1 Hz and an oscillation amplitude of 15 μ m. DMTA measurements were performed by heating samples from -100°C to + 250°C at a heating rate of 5°C/min. Each membrane composition was tested by quadruplicate on samples 3.5 mm width and 7.0 mm length, thickness was measured for each specimen previous to each experiment.

2.4. Propylene carbonate uptake

The propylene carbonate (PC) uptake ability of the polymer electrolytes was investigated at room temperature under argon atmosphere inside the glove box. Blend membranes were previously dried overnight at 50°C under vacuum. Afterwards, they were weighted and later soaked in PC during a controlled time (3 minutes and 1 hour). Once excess solution at the polymer electrolyte surfaces was removed, the wet membranes were weighted once again. The solution uptake was determined using the following expression:

$$PC \text{ uptake}(\%) = \frac{W - W_0}{W_0} \times 100 \quad (\text{Equation 1})$$

where W_0 is the weight of the dried blend membrane and W is the equilibrium weight of the wet membrane after absorbing the PC.

2.5. Ionic conductivity measurements

The evaluation of the electrical behavior of the polymer electrolytes was carried out by AC Impedance Spectroscopy (IS) using an Impedance/Gain-Phase Analyzer SI1260 (Solartron, UK) in the frequency range from 1 Hz to 10 MHz. Impedance measurements were performed by applying a 100 mV amplitude signal at different temperatures while heating (20°C - 90°C). For this purpose, polymer electrolytes were sandwiched between stainless steel blocking electrodes ($\Phi=11$ mm) embedded in a Swagelok-Nylon cell introduced in a programmable climatic chamber (BINDER, Germany). To obtain reproducible measurements, we established a dwell time of 15 minutes before taking every measurement, this time was enough for the system to reach a stable temperature.

3. Results and Discussion

3.1. SPSU-Na – POE electrolytes

3.1.1. X-Ray diffraction (XRD)

The structural properties of SPSU-Na – POE electrolytes, were investigated by XRD. Figure 1 presents the XRD patterns corresponding to samples with different O/Na ratios, all of them recorded at the same experimental conditions. SPSU-Na free of POE presents a XRD pattern with a very wide, weak diffraction peak located at a 2θ value of about 17° , whose morphology indicates the very low crystallinity of this component. Nevertheless, when combined with POE to produce blends with different O/Na ratios, sharp diffraction peaks corresponding to POE, mainly two relatively broad peaks at $2\theta = 19.09^\circ$ and 23.23° [28], overlapped the original SPSU-Na pattern, indicating a semi-crystalline behavior.

From these analyses, performed at room temperature, two significant conclusions can be drawn. On one hand, the incorporation of POE into the SPSU-Na structure produces neither new peaks, additional to both materials, nor a shift with respect to the original

SPSU-Na and PEO peaks. This suggests the immiscibility between both components. On the other hand, considering only the two most significant diffraction peaks of PEO, a clear trend in peaks intensity can be established. The lower the O/Na ratio, the lower the intensity of those diffraction peaks, suggesting a decrease in crystallinity.

Obviously, increasing salt concentration results in a decrease in POE content. Even though, XRD is not quantitative, the diffraction peak seems to decrease more than the impoverishment in POE. This might be related to a slight increase of the polymer chain disorder, which in turn promotes a more amorphous structure.

3.1.2. Thermal and thermomechanical behaviors

3.1.2.1. Thermogravimetric analysis (TGA)

The thermal stability of the polymer electrolytes was investigated by TGA. Figure 2 shows the TGA curves obtained, under nitrogen atmosphere, for the blend components (SPSU-Na and POE) and polymer blends electrolytes with different O/Na ratios. A small weight loss at the low temperature region ($T < 100\text{ }^{\circ}\text{C}$) was observed for all samples, which could be attributed to some water absorption during handling.

Regarding SPSU-Na, two weight losses can be observed; the first one between 420 and 620 $^{\circ}\text{C}$ is related to the degradation of the sulfonic groups (desulfonation process); the second weight loss, which starts at about 650 $^{\circ}\text{C}$, corresponds to the volatilization of main chain's fragments (backbone).

In case of POE, only one major weight loss with an onset temperature (T_{onset}) around 210 $^{\circ}\text{C}$ was observed, and it was completely decomposed at temperatures over 400 $^{\circ}\text{C}$.

Regarding polymer blends electrolytes, three weight losses were noticed. The first one could be attributed to the loss of POE groups, which was delayed (T_{onset} shifted to higher values) to temperature values in between those corresponding to base POE and

SPSU-Na. This could be attributed to a stronger interaction between the sodium ions immobilized in the SPSU structure and the chain fragments of POE originated from thermal degradations. The second and third weight losses correspond to the degradation of SPSU, as described previously. For a reliable battery operation, thermal stability is a highly relevant parameter, since the mechanical properties of the electrolyte are strongly dependent on it. In general, according to TGA results, the lower the O/Na ratio, the higher the thermal stability. In this sense, the polymer blend electrolyte with the highest thermal stability was that with an O/Na=8, in which the first weight loss started at about 285°C, improving the thermal stability in almost 100 °C respect to the pure POE. Indeed, it was previously shown [24] that chain breakings in PSU ionomers start at lower temperatures than these TGA data, but to volatilize these chain fragments must be sufficiently short. So, the relevant information of these analyses is that the resulting blends are sufficiently stable for use in battery and that the volatile and, therefore, flammable fragments are produced at fairly high temperature.

3.1.2.2. Differential scanning calorimetry (DSC)

Polymer blends electrolytes exhibit two well differentiated endothermic peaks at 66 °C and ~105°C, whose associated enthalpy depends on the sodium concentration, i.e. POE content. For simplicity, figure 3 presents only the curve obtained for O/Na=8, besides those corresponding to POE and SPSU for comparison purposes. Interpretation of DSC data, was found very difficult due both to the semi-crystalline nature of POE and of its blending with SPSU-Na. Using the semi-empirical Flory-Fox relationship: $1/T_g = w_A/T_g(A) + w_B/T_g(B)$ where w_A and w_B are the wt fraction of polymer A and polymer B, we calculated the T_g of the blend using two sets of parameters $T_g(A) = 493$ and 573 K (for SPSU-Na) and $T_g(B) = 213$ and 233 K (for POE). For the concentration O/Na =

25, we obtained -22 and $+3$ °C, respectively. We did not observe any glass transition in this temperature range and even in a much broader one. So, we must conclude that POE and SPSU-Na are, in agreement with XRD data, incompatible. This is surprising as POE oligomers, i.e. PEG-400, have been previously used as aid-process plasticizers to extrude SPSU-Na [29,30]. A sharp decrease in T_g and in melt viscosity, in a wide shear rate range, was observed by blending PEG-400 with SPSU-Na proving their perfect miscibility and allowing easy extrusion to be performed. As a first assumption, mixing entropy changes between oligomers and high molecular weight polymers might be invoked. A second one lies in concentration in OH end-groups that interact, *Acceptor Number*, with sulfonate anions and whose concentrations are much higher in PEG-400 than in POE 300,000 g/mole. Last, the previous successful extrusions were performed on SPSU-Na of IEC close to 1.3 meq/g when in this case IEC is equal to 2.5 meq/g.

3.1.2.3. Thermomechanical behavior of polymer electrolytes

Besides providing ionic conductivity, a polymer electrolyte should also withstand high stress during cell packaging and charge/discharge cycling and act as electrical insulator to prevent any short-circuit between electrodes. Moreover, polymer electrolytes with high storage modulus (E') allow the attainment of thinner films, decreasing the electrolyte cost and increasing ionic conductance by reducing the ohmic resistance of the electrochemical cell.

To study the storage modulus E' not only at ambient temperature, but also in the battery operating temperature range, DMTA studies were performed. Figure 4 illustrates the effect of temperature on the storage modulus (E') and $\tan \delta$, starting from -100°C . For clearance, only curves corresponding to $O/Na=25$ are presented, since a similar behavior was observed for the rest of blend formulations.

Obviously, in the vitreous domain, E' increase with the salt concentration i.e. with the decrease in POE content (plot B). Due to the presence of POE, E' starts to decrease from about -50°C . It is noteworthy that E' (i) exceeds 50 MPa at 80°C while in our previous works [14], most of our POE/Na salts exhibited, at 80°C , E' close to 3 MPa and (ii) approaches 10 MPa at 100°C when E' drops down to some KPa from 85°C , in our previous polymer electrolytes. This gain in mechanical strength is appreciable in view of further swelling by liquid solvents or ionic liquids.

Regarding $\tan \delta$, two maxima were noticed for all polymer electrolytes. The first broad peak, appeared at about -40°C ; corresponds to the glass transition temperature of POE [31]. The second $\tan \delta$ maximum does not reflect a second glass transition temperature as POE and SPSU-Na are incompatible. On the other hand, it reflects the creeping of the blend occurring around 105°C .

3.1.3. Ionic conductivity

The ionic conductivity was studied as a function of Na concentration and as a function of temperature. Firstly we analyzed the conductivities of solvent free Na-SPSU-POE blends and later following their swelling in polypropylene carbonate (PC).

a) Conductivities of solvent-free SPSU-Na-POE blends

Conductivities measured at room temperature were, in general, rather poor (ranging from $1.4 \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$) and useful values were obtained only when temperature was beyond POE melting temperature, T_m , i.e. in its amorphous state. Therefore, and as an example, figure 5A shows the Nyquist plots obtained at different temperatures (60 - 90°C) for the highest Na concentration, $\text{O}/\text{Na} = 8$ (a similar behavior was observed for polymer blends electrolytes with different O/Na ratios). This curve exhibits a semicircle

at the high frequency region, related to the bulk conductivity of the polymer electrolyte [32], and a spike at the low frequency zone associated to the blocking of ions at metal electrodes (non-ionic conductors) [33].

Between 60°C and 90°C, very poor conductivities were achieved, from $1.4 \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ at 60°C (O/Na=12) to $3.1 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ at 90°C (O/Na=8). These dramatically low conductivities unfortunately confirm the POE/SPSU-Na incompatibility suspected from XRD, DSC and DMTA. Conductivities ranging between $5 \cdot 10^{-7}$ and 10^{-6} S/cm at 90°C were reported for a series of SPSU-Li co-crosslinked with POE end-capped by glycidyl moieties. In that case even if SPSU-Li and polyether were incompatible, they were covalently bonded and additionally could benefit from OH functions generated by the epoxy crosslinking [34].

b) Conductivities of SPSU-Na-POE blends swelled by propylene carbonate, PC

Useless as solvent-free polymer electrolytes, it was interesting to assess the conductivity of these Na-rich polymer blend membranes, after immersion in PC. Liquid at temperatures between -49 and +242°C, PC will allow both, increasing cation mobility at sub-ambient temperatures and, due to its high dielectric constant, i.e. 64, increasing ion-pair dissociation. The membranes composed of SPSU-Na and POE, were immersed in PC during a controlled time established at 3 minutes in a glove box, since longer times lead to a partial dissolution of POE in PC and to a significant decrease in mechanical performance. For such polymer electrolytes, a PC uptake up to 30 wt% was obtained. The temperature dependent conductivity of the polymer blends electrolytes immersed in PC, with different Na content is depicted in figure 5B. Unlike PC-free electrolytes, in this case, the addition of PC produced a remarkable enhancement in ionic conductivity over the whole temperature range. Table 1 gathers conductivity values obtained at 30°C,

60°C and 90°C for all electrolytes with different O/Na ratios. In this case, the electrolytes provided conductivity values with improvements ranging up to 2.5 times. As a matter of fact, most relevant results were observed at room temperature, where conductivity increased from 4 to 5 orders of magnitude. At 30°C, the highest conductivity was obtained for the concentration O/Na=12 ($2.0 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$), just followed by O/Na=16 ($1.6 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$). At the highest tested temperature, 90°C, conductivity reached values up to $0.06 \text{ mS} \cdot \text{cm}^{-1}$ for O/Na=20.

As the *Donor Number* (DN) of PC is lower than that of POE, its neat contribution to conductivity cannot be mainly ascribed to PC solvating properties but rather to its dielectric constant and to its cation mobility contribution. It can be inferred that, due to POE \leftrightarrow SPSU-Na immiscibility, solvation by POE of Na⁺ of contact ion-pairs is almost impossible. On the other hand, PC increases the ion-pair dissociation allowing Na⁺ to be solvated by POE chains by itself or by both. Once the ion-pairs dissociated, PC will mainly ensure the cation mobility. These conductivities are lower than those reported by Keuer et al.[35], but these ones were obtained (i) by using DMSO, which is not suitable in batteries, and (ii) in solution.

3.2. SPSU-Na – poly PEGMA-PC electrolytes

Given the positive effect on the conductivity of the polymer electrolytes when PC was integrated in the polymer complex, it could be envisioned that higher immersion times would be translated into improved ionic conductivity values. However, the partial dissolution of POE in PC provoked a significant decrease in mechanical properties when higher immersion times were tried, leading to gel-type membranes hardly to be handled. In this sense, to improve mechanical properties of the electrolytes, new

formulations were prepared by substituting linear POE by MONO-PEGMA and DI-PEGMA macromonomers, having functionality of 2 and 4, respectively Both DI-PEGMA and macromonomer mixtures undergo free-radical polymerization, leading to tridimensional polymers. Using this approach, it was planned to increase ionic conductivity by increasing the PC content in the polymer electrolyte (immersion time superior to 3 minutes). In this preliminary study, we selected one concentration (O/Na = 16) and prepared two new compositions: (1) SPSU-Na / poly(DI-PEGMA) and (2) SPSU-Na / poly(MONO+DI-PEGMA) (50/50 wt).

Using these poly-PEGMA polymers instead of POE, higher immersion times were tried. SPSU-Na – DI-PEGMA electrolytes presented a solution uptake up to 19.6 wt% and 75 wt% after 1 hour and 3 hours, respectively. Regarding SPSU-Na – MONO+DI-PEGMA, electrolytes presented a solution uptake up to 99 wt% and 138 wt% after 1 hour and 3 hours, respectively. As expected, the higher the immersion time, the higher the solution uptake. The swelling of the electrolytes by PC was increased up to 1h, without foregoing mechanical stability of the membranes prior to the conductivity measurement. Figure 6 presents the temperature dependent conductivity of both polymer electrolytes. At room temperature (30°C), conductivity values of $1.3 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ and $1.4 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ for DI-PEGMA and MONO+DI-PEGMA were obtained, respectively. As temperature increased, also ionic conductivity did, presenting values of about $8.7 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ and $4.1 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 90°C for DI-PEGMA and MONO+DI-PEGMA, respectively. As expected, MONO+DI-PEGMA offers considerably better results of ionic conductivity regarding DI-PEGMA, with maxima values one order of magnitude higher. This can be associated to a decrease in cross-link density, which favors ions mobility and increase PC uptake. To evaluate the effect of immersion time in ionic conductivity, additional samples were swelled overnight. However, no

significant improvements were observed. Even though the cationic transport number should be equal to 1 (entangled SPSU-Na chains), the cationic conductivities $\sigma \cdot T^+$, assuming $T^+ = 1$, are about 1 order of magnitude lower than those of a set 'liquid electrolyte'/macroporous separator.

3.3. SPSU-Na – poly PEGMA swelled by NaClO₄/PC electrolyte

NaClO₄ is among the less expensive and the most performing sodium salt both in liquid and polymer electrolytes. Nevertheless, due to safety concerns, its use in rechargeable batteries remains questionable. As our membranes are Na-rich, we added a very low NaClO₄ amount as compared to usual salt concentrations in battery electrolytes close to 1 mol/l. Thus, a very small concentration of NaClO₄ (O/Na=40) was added to the electrolyte complexes composed of SPSU-Na DI-PEGMA semi-IPN. Such a low concentration was selected on the basis of not to introduce hazardous products into the polymer electrolyte, trying to maintain standard safeties. Hence, according to the SPSU-Na content, the sodium perchlorate one reaches 1.3 or 1.7 wt%, which is considerable lower when compared to ~12 wt% in a conventional liquid electrolyte.

These polymer electrolytes including NaClO₄ presented a solution uptake up to 241 wt%. As seen in figure 7, conductivities significantly increased upon NaClO₄ incorporation reaching values from 0.1 mS·cm⁻¹ to 0.4 mS·cm⁻¹ for room temperature and 90°C, respectively. These results represent more than one order of magnitude in ionic conductivity improvement and even though T^+ should be lower than 1, no concentration gradient should be feared as the ionomer is intimately entangled with the polyether chains. The obtained conductivities approach those reported by Lu et al. [36] for a polycondensate alternating non-ionic polysulfone blocks with POE oligomer ones, blended with LiTFSI (at the concentration O/Li = 8) and swelled by succinotrile.

However, LiTFSI was used in much higher concentration than NaClO₄, in this study, as the polysulfone blocks were non-ionic.

4. Conclusions

The blends and semi-interpenetrated networks made of SPSU-Na ionomers with respectively linear and cross-linked polyethers, were found incompatible and exhibited insignificant ionic conductivities. However SPSU-Na delays the polymer electrolyte creeping. The presence of SPSU-Na component delays too the weight loss onset of POE, improving the thermal stability of the macromolecule, by almost 100 °C, for the sample with the highest Na content. Deceiving conductivities were obtained for the solvent-free polymer electrolytes.

However, once swelled by propylene carbonate, their conductivities sharply increase but remain still insufficient to be used as polymer electrolytes in Na-batteries. On the other hand, the swelling of the semi-interpenetrated networks by NaClO₄/PC solutions allows reaching competitive conductivities with respect to the State Of the Art. Although the use of perchlorate salts is questionable, this very low content might be acceptable.

These preliminary results deserve to be completed by varying the ionic function, the polyether network, the added sodium salt.

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FIGURES

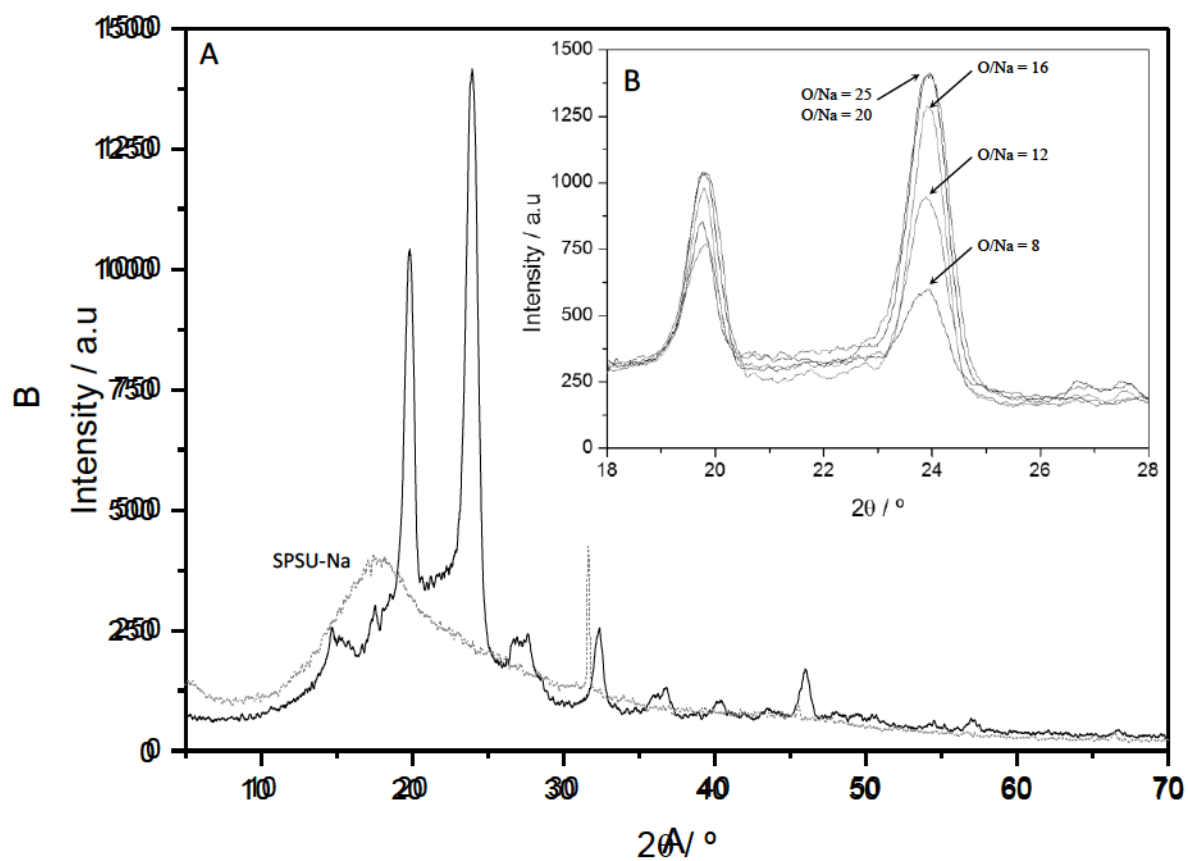


Figure 1. X-Ray diffraction patterns of SPSU-Na (dash line) and SPSU-Na – POE electrolyte (O/Na = 25; continuous line). In the inset a zoom-in of the main diffraction peaks area (at $2\theta \sim 19^\circ$ and 23°) for samples with different O/Na ratios (8 – 25).

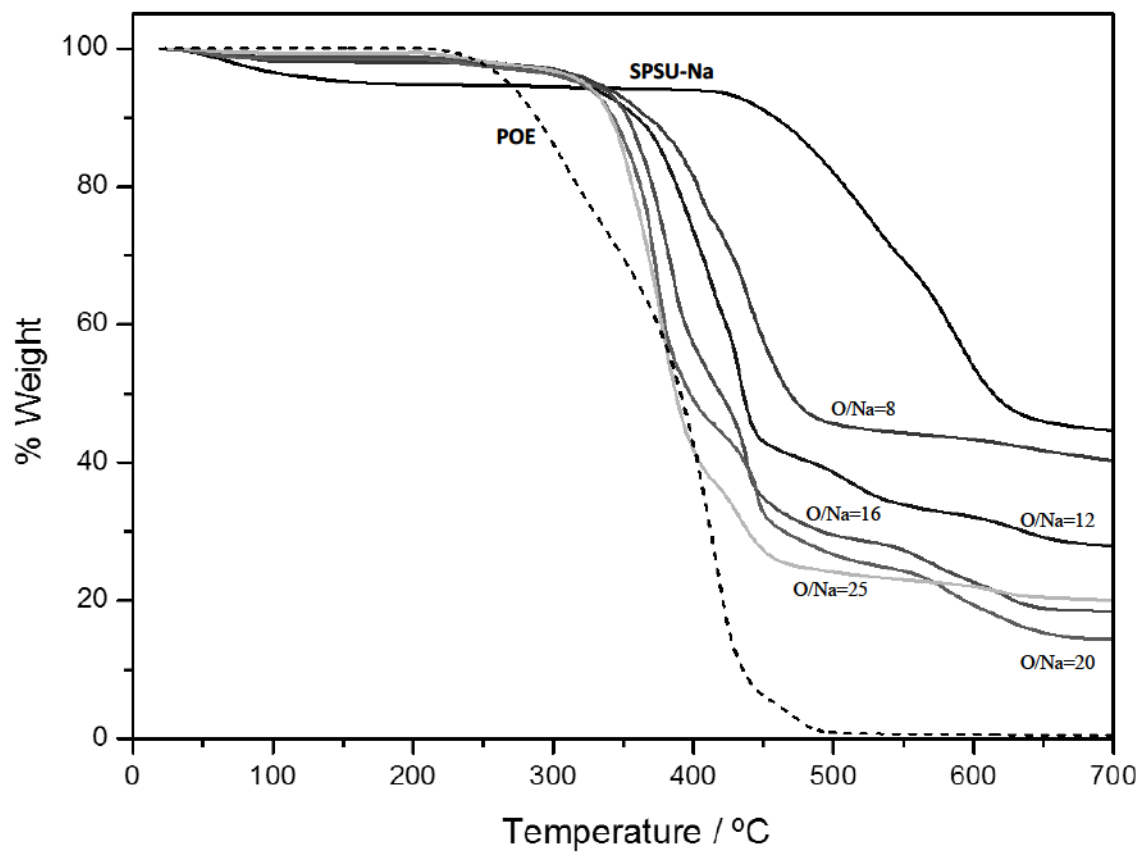


Figure 2. TGA thermograms of SPSU-Na, POE and their blends (SPSU-Na - POE) with different O/Na ratios.

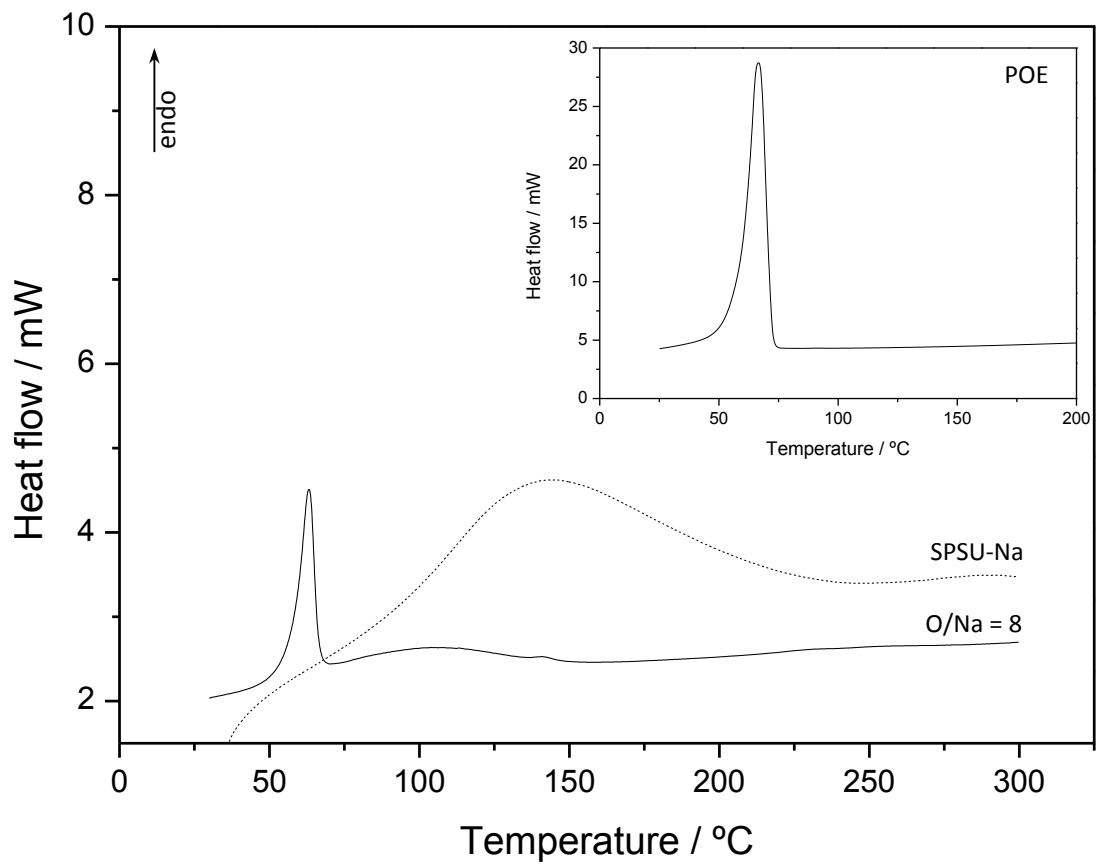


Figure 3. DSC curves obtained for SPSU-Na (dash line), SPSU-Na + POE for O/Na=8 (continuous line) and POE (inset).

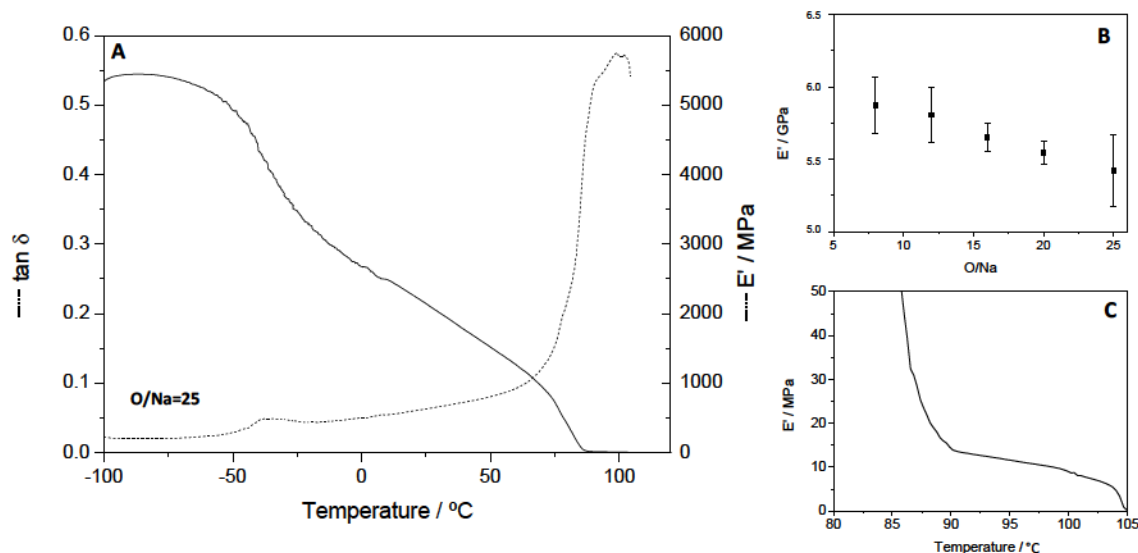


Figure 4. A: DMTA curves of SPSU-Na – POE (O/N a=25). B: standard deviation bars (n=4) of the maximum storage modulus for different O/N a ratios. C: Zoom-in beyond melting temperature for E' .

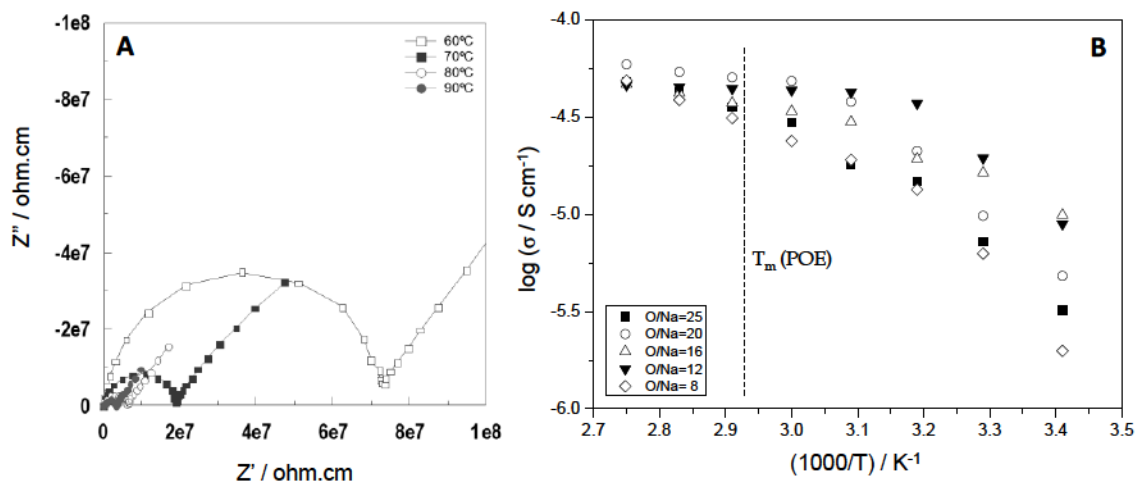


Figure 5. A: Nyquist plots obtained for a polymer electrolyte with O/N a=8. B: temperature dependence of ionic conductivity for all polymer electrolytes once immersed in PC during 3 minutes.

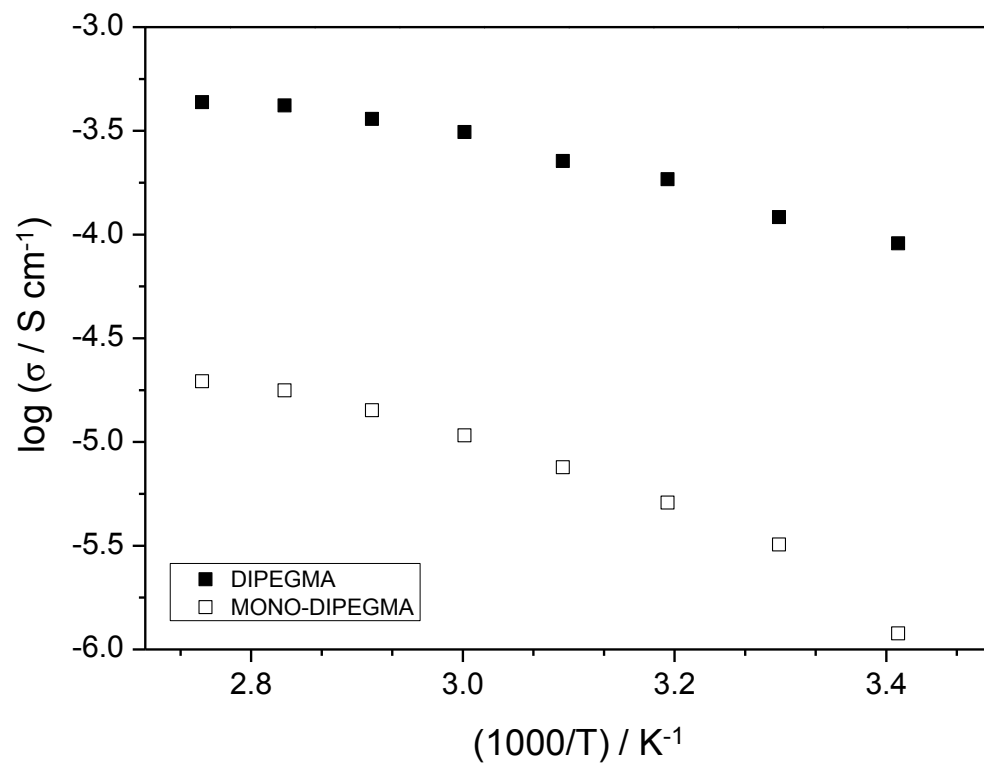


Figure 6. Evolution of bulk conductivity with temperature of polymer blend electrolytes based on SPSU-Na and PEGMA polymers (O/Na=16) after immersion in PC during 1 hour.

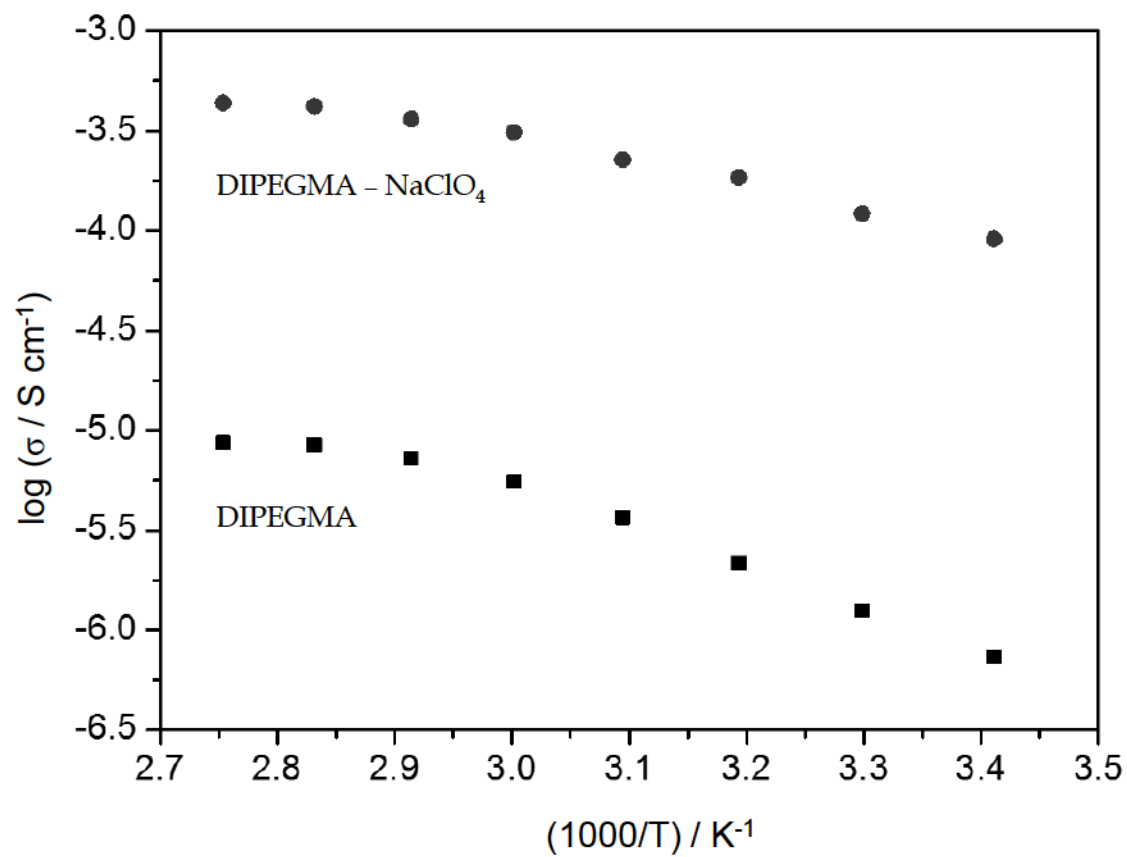


Figure 7. Effect of NaClO₄ (O/Na=40) on conductivity of polymer electrolytes composed of SPSU-Na, DIPEGMA and PC at different temperatures.

Table 1. Ionic conductivity at 30°C, 60°C and 90°C for all SPSU-Na-POE electrolytes:
PC-free and after immersed in PC.

O/Na	σ Conductivity / S·cm ⁻¹)					
	PC-free electrolytes			Electrolytes swelled by PC		
	30°C	60°C	90°C	30°C	60°C	90°C
8	5.6 x10 ⁻¹¹	1.3 x10 ⁻⁸	3.1 x10 ⁻⁷	6.3 x10 ⁻⁶	2.4 x10 ⁻⁵	4.9 x10 ⁻⁵
12	7.2 x10 ⁻¹¹	1.4 x10 ⁻⁸	9.5 x10 ⁻⁸	2.0 x10 ⁻⁵	4.4 x10 ⁻⁵	4.6 x10 ⁻⁵
16	1.9 x10 ⁻¹⁰	6.3 x10 ⁻¹¹	8.9 x10 ⁻⁸	1.6 x10 ⁻⁵	3.4 x10 ⁻⁵	4.7 x10 ⁻⁵
20	5.1 x10 ⁻¹⁰	1.4 x10 ⁻⁹	1.6 x10 ⁻⁷	9.8 x10 ⁻⁶	4.9 x10 ⁻⁵	5.9 x10 ⁻⁵
25	6.2 x10 ⁻¹⁰	2.9 x10 ⁻¹⁰	1.1 x10 ⁻⁷	7.2 x10 ⁻⁶	3.0 x10 ⁻⁵	4.8 x10 ⁻⁵