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Miguel, Álvaro; Fornari, Rocco Peter; García, Nuria; Bhowmik, Arghya; Carrasco de Busturia, David; García Lastra, Juan Maria; Tiemblo, Pilar

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Understanding the molecular structure of the elastic and thermoreversible AlCl_3 :urea/polyethylene oxide gel electrolyte

Álvaro Miguel,^[a] Dr. Rocco Peter Fornari,^{*[b]} Dr. Nuria García,^[a] Dr. Arghya Bhowmik,^[b] Dr. David Carrasco-Busturia,^[b] Prof. Juan Maria García-Lastra^[b] and Dr. Pilar Tiemblo^{*[a]}

[a] Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC)
Calle Juan de la Cierva 3, 28006 Madrid, Spain
E-mail: ptiemblo@ictp.csic.es

[b] Department of Energy Conversion and Storage (DTU Energy)
Technical University of Denmark
Anker Engélunds Vej, Building 301, 2800 Kongens Lyngby, Denmark
E-mail: rocfor@dtu.dk

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Abstract: It is possible to prepare elastic and thermoreversible gel electrolytes with significant electroactivity by dissolving minimal weight fractions of Ultra High Molecular Weight poly(ethylene oxide) (UHMW PEO) in an aluminum deep eutectic solvent (DES) electrolyte composed of AlCl_3 and urea at a molar ratio of 1.5:1 (AlCl_3 :urea). The experimental vibrational spectra (FT-IR and Raman) provide valuable information on the structure and composition of the gel electrolyte. However, the complexity of this system requires computational simulations to help interpretation of the experimental results. This combined approach allows us to elucidate the speciation of the DES liquid electrolyte in the gel and how it interacts with the polymer chains to give rise to an elastic network that retains the electroactivity of the liquid electrolyte to a very great extent. The observed reactions occur between the ether in the polymer and both the amine groups in urea and the aluminum species. Thus, similar elastomeric gels may likely be prepared with other aluminum liquid electrolytes, making this procedure an effective way to produce families of gel aluminum electrolytes with tunable rheology and electroactivity.

Introduction

Batteries are at the heart of the present and future energy management strategy;^[1] for light and portable devices, for powering electric vehicles, to store energy from renewable sources, and to optimize the electrical grid management. Each application has its requirements: some need low-cost batteries, other high energy/power density batteries, or batteries that are shapeable. Hence many different battery technologies for different market niches have been developed. Lithium is the lightest metal with the lowest reduction potential (-3.045 V vs. NHE), which makes it excellent for metal battery technologies, but it is relatively scarce.^[2] Aluminum is the most abundant metal on earth's crust, and its volumetric capacity of 8040 mAh cm^{-3} is almost four times higher than lithium (2046 mAh cm^{-3}).^[3] It dates back to 1948 when the first electroplating bath was patented. It consisted of a mixture of the room temperature ionic liquid (RTIL) N-alkyl pyridinium halide and aluminum chloride with molar concentration 1 to 2.^[4] More recently, deep eutectic solvents (DES) obtained from AlCl_3 :amide mixtures with different ratios have proved to be excellent electrolytes for aluminum secondary batteries. DES are environmentally friendly and have the same

benefits as RTILs (low vapor pressure, tunability, easiness to prepare), at a much lower price.^[5]

One of the major requirements of batteries nowadays is safety. As these devices are becoming ubiquitous, it is compulsory to eliminate the risks of toxic liquid leaks or short-circuit and subsequent explosions, thermal runaway, or other safety hazards. Solid electrolytes are much safer than liquid ones, avoiding leaks and eliminating or mitigating short-circuiting due to dendrite growth or mechanical stress, but have lower diffusivity, together with a poor electrode/electrolyte contact.^[6] Polymer gel electrolytes (PGEs) may combine the advantages of liquid and solid electrolytes, providing sufficient ion mobility, avoiding leaks, mitigating dendrite growth, and acting as separators.^[7] Scarce examples of PGEs with an aluminum electrolyte suitable for secondary batteries have been reported to date.^[7-8] They are obtained by in-situ polymerization of the monomer acrylamide, using azobisisobutyronitrile (AIBN) as initiator. The liquid electrolytes used consist of 1-ethyl-3-methylimidazolium chloride (EMImCl) and AlCl_3 (EMImCl: AlCl_3 , 1:1.5, in molar ratio), or triethylammonium chloride (Et_3NHCl) and AlCl_3 (1:1.6 molar ratio) with an 80 wt % of ionic liquid. These polymer gel electrolytes are prepared with the help of an auxiliary solvent, which promotes the dissolution of the polymer and its mixing with the electrolyte's liquid phase. In the case of the gels mentioned above, the chosen solvent was dichloromethane. The choice of the solvent for membrane casting for aluminum electrolytes is not straightforward, as highly interactive strong Lewis acids are present in them, namely AlCl_3 and Al_2Cl_7^- , produced in the presence of an excess of AlCl_3 . Indeed, the electrochemical activity of Al electrolytes (EMImCl/ AlCl_3 in particular) decreases when diluted with solvents bearing lone electron pairs such as acetone, acetonitrile or tetrahydrofuran (THF).^[6]

As a rule, the elimination of auxiliary solvents in all kinds of processes is an endeavor of materials scientists in search of more sustainable and scalable procedures. Apart from not being environmentally friendly, auxiliary solvents are a drawback in any chemical process. Getting completely rid of the solvent is not a simple task, frequently involving heating steps, which makes solvent casting cumbersome and lacking the reproducibility that solvent-free processes have, which makes mass production complicated.

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In a recent work,^[9] we proposed a solvent-free strategy consisting of the melting while mixing of poly(ethylene oxide) (PEO) in AlCl_3 :urea electrolyte to prepare PGEs. Deep eutectic solvents prepared with AlCl_3 and urea at molar ratio of 1.5:1 (called U150 hereafter), have proved to be an excellent medium for the electrodeposition of aluminum.^[10] We showed how the use of ultra-high molecular weight PEO (MW > 10^6 g/mol) allows the preparation of gels where reasonable mechanical properties are attained while electrochemical activity is retained (even though molecules with lone electron pairs are known to interact with the aluminum species, thereby changing the speciation and deteriorating the electrochemical activity).^[6] The amount of PEO necessary to obtain a gel is extremely low, and it is lower for higher molecular weight. Producing a gel can only be possible if there is a strong interaction between ethylene oxide (EO) units and U150. This interaction must be mainly physical, given the observed thermoreversibility.

As the speciation of aluminum electrolytes is still unknown, unraveling the nature of the interactions between PEO and U150 is not an easy task. U150 is believed to be formed by the heterolytic rupture of AlCl_3 oligomers and formation of Al-O bonds between Al and urea to obtain $[\text{AlCl}_2\text{urea}_2]^+$ and AlCl_4^- . The Lewis acidic medium (AlCl_3 molar ratio > 1) promotes the formation of anionic species like Al_2Cl_7^- , produced in the presence of an excess of AlCl_3 . Both cationic $[\text{AlCl}_2\text{urea}_2]^+$ and anionic Al_2Cl_7^- have been proposed to be directly related to the electrodeposition of Al in the negative electrode^[11] as described by the following reactions:

There is controversy about the preferred mechanism. The dissociation energy of the aluminum species suggests that the mechanism involved in reaction [1] should be more favorable,^[12] but not only thermodynamic factors are involved in these complex electrochemical processes.

This work is devoted to the understanding of the structure of the U150/poly(ethylene oxide) gel by combining experimental vibrational spectroscopy and computational chemistry.

Results and Discussion

In this work, the studied PGE is named PEO50-1/U150. This nomenclature stands for 1 wt % of PEO with molecular weight 50×10^5 g mol⁻¹ (PEO50-1), and 99 wt % of the deep eutectic solvent U150. The gel PEO50-1/U150 is prepared by mixing the powdery PEO with U150 and stirring the mixture while increasing the temperature up to 70 °C. When the polymer melts, viscosity increases conspicuously because of the mixing of the long polymer chains with the deep eutectic solvent.^[9] This preparation process takes a few minutes and requires no other steps, contrary to procedures where auxiliary solvents are used. As the gel cools down to room temperature, it becomes a very soft gel with an elastomeric character. Figure S1 collects a qualitative characterization of its rheological and mechanical behavior. Figure S1a shows the result of the inverted tube test: PEO50-1/U150 does not flow when inverting the tube, but it is seen to creep down the walls of the tube slowly, and after 10 minutes,

clear deformation of the gel is seen. Creep is also observed at the center of the beaker, not just down the walls. A representation of this behavior appears in the drawing in Figure S1a, as the photo was not clear enough. When manipulating this sample, an elastic character is detected, and simple stretching tests were carried out inside the glovebox to illustrate it. Figure S1b collects images showing the elasticity of PEO50-1/U150, which can also be seen well in the video included in Figure S1c. Because of the large deformation attained by this elastic gel, it can be described as an elastomer. This gel is also very sticky, especially to itself, and in comparison with neat U150 it is much less sensitive to moisture, which is a clear advantage when handling it. Finally, if heated at temperatures close to 70 °C, the viscosity of the gel decreases, and it increases again on cooling, being thus a thermoreversible gel.

Characterization of the concentration of Al_2Cl_7^- and AlCl_4^- species is very relevant in this type of electrolytes, and probably the most apt technique to characterize it is Raman spectroscopy. The Raman spectra of AlCl_3 :urea DES with different ratios of urea and AlCl_3 have been thoroughly studied by other authors.^[13] The AlCl_3 Raman spectrum shows peaks at 274, 380 and 492 cm⁻¹, while Al_2Cl_7^- peaks are assigned at 312 and 433 cm⁻¹ and AlCl_4^- peaks at 349 cm⁻¹. Figure 1a shows the Raman spectra of U150 and PEO50-1/U150. The spectra show that only minimal amounts of AlCl_3 aggregates appear. In both samples, the most conspicuous bands in the low-frequency region are at 312 and 349 cm⁻¹, corresponding respectively to Al_2Cl_7^- and AlCl_4^- . However, the relative intensity of the band at 312 cm⁻¹ with respect to the 349 cm⁻¹ band is higher in U150 than in PEO50-1/U150. In fact, if we compare the relative intensity of the bands at 312 and 349 cm⁻¹ with that of Raman in other publications^[11b] on AlCl_3 :urea DES, it is found that PEO50-1/U150 resembles the DES with concentration AlCl_3 :urea 1.3:1 rather than the DES with concentration 1.5:1, which is the one used to prepare PEO50-1/U150. Thus, the gelling of U150 with PEO does decrease the Al_2Cl_7^- concentration with respect to AlCl_4^- , but it is still in the range of other less acidic DES, such as U135.

Figure 1. Raman spectrum of U150 (black) and PEO50-1/U150 (red) showing the peaks assigned to $(\text{AlCl}_3)_n$ in red, Al_2Cl_7^- in green, and AlCl_4^- in blue. In the inset, CV of U150 and PEO50-1/U150, same color code (Cycle number 40).

It has been proposed that the higher the concentration of the acidic Al_2Cl_7^- as compared to the basic AlCl_4^- , the higher the

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electrodeposition ability of the aluminum electrolyte.^[11b] The cyclic voltammetry (CV) of the gel and the liquid electrolyte appears as an inset in Figure 1. The oxidation and reduction peaks of the gel are very similar to those in the liquid U150, and the plating current density at -0.8 V decreases by 35% from $j = 2.6$ mA cm⁻² in U150 to $j = 1.7$ mA cm⁻² in PEO50-1/U150. As for ionic conductivity (σ) PEO50-1/U150 has a $\sigma = 6.2 \times 10^{-4}$ S cm⁻¹ at 25 °C, in comparison with $\sigma = 7.6 \times 10^{-4}$ S cm⁻¹ of pure U150, a decrease of 18%. The stripping/plating ability of the gel electrolyte, as characterized by j , decreases more than its σ . This is so because not only is viscosity increasing but also the interaction of U150 with PEO reduces the concentration of Al_2Cl_7^- with respect to AlCl_4^- , as reflected in the Raman spectra of Figure 1. Nonetheless, both the concentration of Al_2Cl_7^- in the Raman spectrum and the j of PEO50-1/U150 mildly decrease in comparison with the pure U150.

We have shown that the PEO50-1/U150 gel retains the electroactivity of U150 and enhances its mechanical properties and moisture resistance. Designing strategies to improve these gels further requires gaining knowledge of their microscopic structure. This task involves understanding how crosslinks are formed, which species are involved, and which chemical changes are produced in the speciation of the liquid electrolyte. Since the speciation of U150 itself is not unmistakably known, this task is far from simple. In the following, a computational investigation of the gel and its validation with FT-IR spectroscopy is performed.

Ab initio calculations can help to identify the main species present in U150 and their possible interactions with PEO. It is known from multiple studies^[11b, 12, 14] that the main species thought to be present in AlCl_3 :urea DES are the anions Al_2Cl_7^- and AlCl_4^- , the cations $[\text{AlCl}_2(\text{urea})_2]^+$ and $[\text{AlCl}_2(\text{urea})]^+$, and the neutral species $(\text{AlCl}_3)_n(\text{urea})$ with $n=1,2,3$. Furthermore, we also take into account the possible formation of a larger cation: $[\text{Al}_2\text{Cl}_5(\text{urea})_2]^+$ where the two urea molecules can be bonded either to the same Al or to two different Al. The structures of these species are shown in Figure 2. We considered bonds between the Al and the O and N atoms in the urea units. We found that species with Al-N bonds are significantly less stable than those with Al-O bond. Thus, we do not show species with Al-N bonds in Figure 2.

Figure 2. Optimized geometries of the main species in AlCl_3 :urea DES.

It is well known that urea forms hydrogen bonds with the oxygen atoms of PEO in the so-called inclusion compounds,^[15] and we find that the preferred geometry for this bonding is with the plane of urea orthogonal to the PEO chain as illustrated in Figure 3. In this geometry, two of urea's hydrogens point towards the two lone pairs of PEO's oxygen.

Figure 3. Optimized geometry of one urea molecule hydrogen-bonded to a methyl-terminated triethylene glycol (TEG) oligomer.

Therefore, all the cations shown in Figure 2 can potentially form crosslinking between EO units. The hydrogen bond between the urea belonging to the cation $[\text{AlCl}_2(\text{urea})_2]^+$ and the EO unit is expected to be stronger than that between free urea and an EO unit, because of the larger partial positive charge residing on the hydrogens in the cation. This is confirmed by the computed bonding energies (i.e., the energy of the bonded complex relative to the sum of the energies of its isolated molecular constituents) of -0.69 eV and -0.45 eV, respectively. Moreover, the oxygen atoms belonging to PEO are also Lewis bases (although weaker than urea's oxygen), so in principle, they can also bond to acid Al species.

To test these ideas, we examine several model structures, shown in Figure 4, with the same overall chemical formula $(\text{Et}_2\text{O})_2\text{Al}_3\text{Cl}_3(\text{urea})_2$, making their electronic energies directly comparable as they have the same number of atoms. Diethyl ether (Et_2O) is a minimal model for the EO units of PEO, allowing to represent its local chemistry at a low computational cost. The chemical formula given above reflects the molar ratios of AlCl_3 and urea in U150, while the actual molar fraction of the EO units in PEO50-1/U150 would be much lower (0.023). Nevertheless, examining the reactions between these model systems can help to identify the most likely local interactions between PEO and U150. In Figure 4, models A-D are the reactants, i.e. species present in pure U150, to which the energy of two isolated Et_2O units (in solution) was added, and models 1-5 are possible products resulting from interactions between Et_2O and U150 species. More specifically, these interactions are hydrogen bonds between urea and Et_2O oxygens and Al-O bonds formed by acid-base reactions between Al species and Et_2O . Since the ranges of electronic energies obtained are just ~ 0.3 eV for the reactants and ~ 0.2 eV for the products, we assume that they can all coexist in the real PGE. In model 1, the Et_2O units are bound to neutral species that cannot form chemical crosslinking, while in models 2-5 cationic species form crosslinking between EO units. In Table 1 we report the reaction energies $\Delta E = E_{\text{products}} - E_{\text{reactants}}$ of selected reactions. The reactions labelled X and Y, which do not form crosslinking, have different stoichiometry but are also relevant and involve neutral species already included in the other models. We have considered all possible reactant and product combinations obtainable from the species shown in Figure 2, but report in Table 1 only those which are both thermodynamically

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favorable (negative ΔE) and kinetically favorable. Using qualitative criteria, reactions involving many steps or where Al-O bonds are broken are considered kinetically unfavorable and are not shown in Table 1. The reactions $D \rightarrow 5$, $B \rightarrow 3$ and $A \rightarrow 4$ are kinetically the most favorable since they simply involve the formation of hydrogen bonds without any other bonds forming or

breaking. All other reactions involve, in addition to hydrogen bonds, also the breaking of Al-Cl bonds and the formation of Al-O bonds for products 1 and 2. Inter-conversion between reactants 1 and 2 between products 3 and 4 should also be kinetically favorable since it only requires the transfer of one AlCl_3 .

Figure 4. Structures, chemical formulas and electronic energies of selected species in U150 (+ not interacting Et_2O) (top) and PEO50-1/U150 (bottom) with chemical formula $(\text{Et}_2\text{O})_2\text{Al}_3\text{Cl}_9(\text{urea})_2$ optimized at the B3LYP-D3(BJ)/ADZP level of theory with the COSMO implicit solvation model. All energies relative to product 1.

Table 1. Energy changes in selected reactions between Et_2O and U150 species. The structures are shown in Figure 4.

Label	Reactants	Products	ΔE / eV
D $\rightarrow$ 2	$2 \text{Et}_2\text{O} + [\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{diff. Al}) : \text{AlCl}_4^-$	$[(\text{Et}_2\text{O})_2\text{AlCl}_2(\text{urea})]^+ : \text{AlCl}_4^- + \text{AlCl}_3(\text{urea})$	-1.327
X	$2 \text{Et}_2\text{O} + 2 \text{Al}_2\text{Cl}_6(\text{urea})$	$2 (\text{Et}_2\text{O})\text{AlCl}_3 + 2 \text{AlCl}_3(\text{urea})$	-1.260
C $\rightarrow$ 1	$2 \text{Et}_2\text{O} + \text{Al}_2\text{Cl}_6(\text{urea}) : \text{AlCl}_3(\text{urea})$	$(\text{Et}_2\text{O})(\text{urea})\text{AlCl}_3 : \text{AlCl}_3(\text{urea}) + (\text{Et}_2\text{O})\text{AlCl}_3$	-1.162
C $\rightarrow$ 2	$2 \text{Et}_2\text{O} + \text{Al}_2\text{Cl}_6(\text{urea}) : \text{AlCl}_3(\text{urea})$	$[(\text{Et}_2\text{O})_2\text{AlCl}_2(\text{urea})]^+ : \text{AlCl}_4^- + \text{AlCl}_3(\text{urea})$	-1.157
D $\rightarrow$ 5	$2 \text{Et}_2\text{O} + [\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{diff. Al}) : \text{AlCl}_4^-$	$[(\text{Et}_2\text{O})_2\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{diff. Al}) : \text{AlCl}_4^-$	-1.139
B $\rightarrow$ 3	$2 \text{Et}_2\text{O} + [\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{same Al}) : \text{AlCl}_4^-$	$[(\text{Et}_2\text{O})_2\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{same Al}) : \text{AlCl}_4^-$	-1.099
A $\rightarrow$ 3	$2 \text{Et}_2\text{O} + [\text{AlCl}_2(\text{urea})_2]^+ : \text{Al}_2\text{Cl}_7^-$	$[(\text{Et}_2\text{O})_2\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{same Al}) : \text{AlCl}_4^-$	-1.006
B $\rightarrow$ 4	$2 \text{Et}_2\text{O} + [\text{Al}_2\text{Cl}_5(\text{urea})_2]^+ (\text{same Al}) : \text{AlCl}_4^-$	$[(\text{Et}_2\text{O})_2\text{AlCl}_2(\text{urea})_2]^+ : \text{Al}_2\text{Cl}_7^-$	-0.968
Y	$2 \text{Et}_2\text{O} + 2 \text{AlCl}_3(\text{urea})$	$2 (\text{Et}_2\text{O})(\text{urea})\text{AlCl}_3$	-0.894
A $\rightarrow$ 4	$2 \text{Et}_2\text{O} + [\text{AlCl}_2(\text{urea})_2]^+ : \text{Al}_2\text{Cl}_7^-$	$[(\text{Et}_2\text{O})_2\text{AlCl}_2(\text{urea})_2]^+ : \text{Al}_2\text{Cl}_7^-$	-0.875

The computational investigation of the speciation and of the possible reactions between U150 species and PEO provides a set of species which can be present in the gels, since their energy

difference is small. To gain further insight into speciation, we compare the FT-IR spectrum of the gel with the calculated IR spectrum. Figure 5 shows the FT-IR spectra of the PEO50-

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1/U150 gel (PGE), U150, PEO, and a PEO:urea 1:1 inclusion compound (IC). As discussed elsewhere,^[9] the most intense FT-IR band of solid PEO is not seen in the PGE, namely the characteristic backbone band centered at 1095 cm⁻¹ assigned to combinations of stretching C-C and C-O, and COC deformation modes, which is very conformationally-sensitive.^[16] However, the CH₂ twisting bands at 1241 and 1278 cm⁻¹, which are far less intense than the 1095 cm⁻¹ band, are hinted in the PGE's spectrum (red rectangle in Figure 5). Other PEO bands do not appear in the PGE's spectrum: the CH₂ rocking at 840 cm⁻¹ and the CH₂ wagging at 1342 and 1360 cm⁻¹. Conversely, the PGE FT-IR displays new bands in the 920-1020 cm⁻¹ region, which do not appear in the FT-IR spectra of either neat U150 or PEO. These bands are proportional to the concentration of PEO in the gel.^[9]

Figure 5 shows some resemblance between the spectra of PEO50-1/U150 and that of the PEO:urea IC, mainly the absence of the PEO backbone band at 1095 cm⁻¹ in both, and the existence in its place of several less intense bands at lower wavenumbers. The similarity between the FT-IR spectra of the IC and the PGE suggests that the PEO chain in the gel is highly constrained as occurs in the IC. The new bands in the 920-1020 cm⁻¹ region, which do not appear in the FT-IR spectra of either neat U150 or PEO, and which have been found to be proportional to the concentration of PEO in the gel, could be new PEO backbone bands. The stiffness of the PEO chains and the appearance of new backbone IR bands may be a consequence of very strong sequential interaction between the repeat units of PEO and U150 species. The existence of such strong interaction could have been foreseen, not only because urea interacts readily with PEO, but also because the electron-deficient AlCl₃ and Al₂Cl₇⁻ tend to interact or react with molecules bearing lone electron pairs, including polymers such as PEO.

Figure 5. FT-IR spectra of pure PEO, PEO50-1/U150 gel, the PEO:urea 1:1 inclusion compound (IC), pure urea and pure U150.

The vibrational frequencies computed in the gas phase for all the species shown in Figures 2 and 4 (all species were calculated separately, i.e., not as ionic pairs) are reported in Figure 6, which can help to interpret the experimental FT-IR spectra of U150 and PEO50-1/U150. In Figure 6, the orange lines are the combined computed frequencies of many species formed from the interaction between U150 and Et₂O, included in models 1-5 in Figure 4. They explain the appearance in the PEO50-1/U150 spectrum of several bands around 800 cm⁻¹, in the region 920-1020 cm⁻¹ and around 1100 cm⁻¹, which were not present either in the experimental spectrum of U150 (black curve) or in the computed spectrum of the U150 species (blue lines). These computed frequencies correspond to different types of stretching of Et₂O connected to urea and Al, and corroborate the hypothesis that the new bands seen in the FTIR spectra of the PGE belong to PEO backbone vibrations involved in strong interactions with the U150 species. Since they explain the difference between the experimental U150 and PGE spectra, they confirm that the species 1-5 shown in Figure 4 are very likely to be present in the PEO50-1/U150 gel.

Figure 6. FT-IR spectra of U150 (black curve) and PEO50-1/U150 (red curve). The computed vibrational frequencies (intensities on the right axis) of the chemical species shown in Figure 2 and Figure 4 are represented by blue and orange vertical lines, respectively.

We will now attempt to draw a more comprehensive picture of the chemical nature and speciation of the U150 DES and the PEO50-1/U150 gel. To explain the decrease of the [Al₂Cl₇⁻]/[AlCl₄⁻] ratio observed in the Raman spectrum (Figure 1) upon the addition of PEO to U150, we will first discuss the reactions taking place in the AlCl₃:urea DES, then extend the discussion to the reactions with PEO. The increase of the [Al₂Cl₇⁻]/[AlCl₄⁻] ratio when the relative concentration of urea decreases can be explained as follows. When the initial AlCl₃:urea ratio is 1.0, the reactions between the Lewis acid AlCl₃ and the Lewis base urea can produce neutral and ionic species:

The anion Al₂Cl₇⁻ may be produced by the following reactions where one chlorine is exchanged, but the presence of Al₂Cl₇⁻ is not observed in the Raman spectrum.^[10]

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The excess of urea resulting from reaction [7] would then break down the Al_2Cl_7^- anions and form AlCl_4^- :

When the AlCl_3 :urea ratio is 1.5, the excess of AlCl_3 makes more likely the formation of Al_2Cl_7^- from the following reactions:

Some of the urea can break down Al_2Cl_7^- to produce neutral species and AlCl_4^- .

The molar fraction of EO units in the PGE is very low (0.023). However, since most of the urea is already bound to Al species, the oxygen lone pairs of the EO units can also act as Lewis base and break down the Al_2Cl_7^- anions, resulting in the change of the $[\text{Al}_2\text{Cl}_7^-]/[\text{AlCl}_4^-]$ ratio observed in the Raman spectrum (Figure 1) when the PEO is added:

A calculation of the energies of reactants and products for the reactions [11] and [12] shows that both are thermodynamically favored with $\Delta E = -0.49$ eV and $\Delta E = -0.12$ eV, respectively.

Some of the reactions listed in Table 1 can also partly explain the decrease of the $[\text{Al}_2\text{Cl}_7^-]/[\text{AlCl}_4^-]$ ratio observed in Raman and CV. Reaction $\text{C} \rightarrow 2$ consumes neutral species to produce crosslinked species and AlCl_4^- ; in reaction $\text{A} \rightarrow 3$, Al_2Cl_7^- is broken down to produce another crosslinked species and AlCl_4^- ; reaction $\text{B} \rightarrow 4$ has the opposite effect, but the species 4 can easily convert to the more stable species 3 by AlCl_3 transfer which would again affect the $[\text{Al}_2\text{Cl}_7^-]/[\text{AlCl}_4^-]$ ratio in the direction observed.

On the basis of the available experimental evidence and the computational investigation, we propose in Figure 7 an exemplary structure of the PGE. The cartoon at the center depicts entangled polymer chains (blue lines) interacting strongly with a fraction of the DES species (highlighted in blue). Around the central sketch, we show the chemical structures of some of the actual interactions likely to take place between the DES and the polymer, based on the computational results illustrated in Figure 4. The crosslinking structures *a* and *b* are mediated by the $[\text{AlCl}_2(\text{urea})]^+$ and $[\text{Al}_2\text{Cl}_5(\text{urea})_2]^+$ cations, which form Al-O and hydrogen bonds with oxygens belonging to different chains or chain sections. Structure *c* shows the possible effect of non-crosslinking neutral species $\text{AlCl}_3(\text{urea})$ and AlCl_3 bonded to the polymer.

Figure 7. Interactions between PEO segments and different AlCl_3 :urea DES (U150) species: structures *a*, *b* and *c* are based respectively on models 2, 3, and 1 of Figure 4. The cartoon in the center illustrates the U150 species (colored circles) and the polymer chains (blue lines). The polymer chain entanglements are blocked by strong interactions with the U150 species (highlighted circles).

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We propose that these strong and extensive interactions, both crosslinking and non-crosslinking, affect most of the EO units given the large molar excess of AlCl_3 :urea DES species. Therefore, they can block entanglements and constrain the free rotation of the polymer chain, explaining the observed changes in the FT-IR spectrum and their peculiar elastomeric behavior. The gels are thermoreversible since most of the interactions have a physical nature. However, if the polymer chain is sufficiently long, it will be entangled with many other chains, and those entanglements will not easily slip when stretched since the extensive interactions and a certain degree of crosslinking will block them. The consumption of Al_2Cl_7^- described in detail in this last section also explains why the addition of PEO produces a larger decrease in the CV current than in the conductivity.

Conclusion

Elastic and thermoreversible gels of AlCl_3 :urea deep eutectic solvent (DES) are prepared using UHMW PEO by a simple procedure consisting of the mixing and melting of the polymer in the liquid electrolyte. As little as 1 wt % of PEO is enough to produce gels that are easy to handle. The gels are sturdy and can be stretched and deformed like a rubber. They are also sticky, which in combination with their elastomeric character, makes them self-healing. CV experiments show that the gel electrolyte largely retains the electroactivity of the liquid AlCl_3 :urea DES. FTIR spectroscopy suggests that the polymer adopts very constrained conformations in the gel. To elucidate the complex structure of the liquid, we used ab initio calculations to interpret the spectroscopic data and to understand the nature of the interactions between the AlCl_3 :urea species and the PEO. Based on these interactions, we proposed in this contribution a detailed molecular picture of the gel's structure, which explains its appealing combination of electrochemical and rheological properties.

Our ab initio simulations show that the interactions occur between the ether oxygens in the polymer and both the amine groups in urea and the aluminum species. This observation leads to suggest that similar gels can likely be prepared with other aluminum liquid electrolytes. Furthermore, understanding how the gel is formed sheds light on how to combine polymers with different chemical structures and morphologies with other aluminum electrolytes to find optimum balances between rheology and conductivity, making this procedure an effective way to produce new families of aluminum gel electrolytes.

Experimental Section

Materials

To prepare the electrolytes, PEO MW = 5×10^6 g mol⁻¹ from Sigma-Aldrich (Missouri, USA) and uralumina 150 (U150), a DES prepared with AlCl_3 :urea at a molar ratio 1.5:1, from Scionix Ltd. (London, UK) were used. urea (99.5%) from Fischer Scientific (New Hampshire, USA) was employed to prepare the inclusion compound (IC) with PEO, which has been used as a reference. All materials were used as received.

Preparation procedure

U150 was placed in a glass beaker on top of a heating plate inside a glovebox under an argon atmosphere ($[\text{O}_2] < 1$ ppm, $[\text{H}_2\text{O}] < 1$ ppm), and PEO powder was added stepwise while stirring with a glass rod and rising the temperature up to 70 °C. As soon as the temperature got close to 60 °C, the change in the viscosity revealed the melting and mixing of the polymer and the PGE formed.

The PEO:urea 1:1 inclusion compound (IC), used as a reference for the interpretation of the FT-IR spectrum of PEO50-1/U150, has been prepared as reported in the literature^[9] by adding the desired quantity of urea to 100 mL of MilliQ water. Under vigorous stirring at 70 °C, 0.5 g of PEO were added stepwise. Once the polymer was dissolved, the mixture was let to cool down at ambient temperature. Then, 10 mL aliquots were frozen for 12 hours at -20 °C and freeze-dried to eliminate the water. The IC obtained were white solids.

Characterization techniques

Vibrational Spectroscopy

FT-IR spectroscopy was used to study the structure of PEO50-1/U150. PEO50-1/U150 was sandwiched between ZnSe windows 2 mm thick inside the glovebox and their IR spectrum was recorded using a FT-IR Perkin-Elmer Spectrum-One, with 10 scans and resolution of 4 cm⁻¹. The FT-IR of pure U150 was recorded in the same way. Raman spectroscopy was carried out using NMR tubes, in a Perkin Elmer System 2000 NIR FT-Raman, with a laser at 1064 nm wavelength. The NMR tube allowed to protect the electrolyte from the ambient and to focus the laser on its surface.

Rheological and mechanical behavior

Because of the sensibility to humidity of PEO50-1/U150, its rheology has been studied only qualitatively inside the glovebox. Two simple procedures have been employed: the tube inversion test, which is often used to characterize polymer gels,^[17] and a simple stretching test. For the tube inversion test, amounts of 5 g were introduced into a beaker or vial, which is then completely inverted. With the aid of a video camera, the sample was observed for time periods of several minutes. For the qualitative stretching evaluation, we take advantage of the sticky character of PEO50-1/U150 and stretch it with the aid of a glass rod.

Conductivity and Electrochemistry

Electrochemistry was evaluated with an Autolab PGSTAT 302 potentiostat/galvanostat. High purity aluminum foil (99.9999% Goodfellow, Huntingdon, UK) was used for both working and counter electrodes in a home-made electrochemical cell. All aluminum electrodes were cut (0.85 cm²) and afterward cleaned in a 10M KOH solution, washed with deionized water, and dried before all measurements. The thickness of the electrolyte in the cell was about 2 mm. Impedance measurements were carried out at an amplitude of 20 mV from 10⁶ to 1000 Hz. Conductivity was obtained from the equivalent circuit obtained after adjusting the Nyquist diagram. For the voltammetry, the same electrochemical cells were used with a third electrode as a pseudo-reference, of the same aluminum and treatment as the others. Cyclic Voltammetry (CV) has been carried out between -1.5 V and 1.5 V vs. Al/Al^{3+} at 20 mV s⁻¹, for about 100 cycles. The current stabilized after about 20 cycles.

Computational details

The geometries of all the molecular systems studied in this work were optimized at the B3LYP-D3(BJ)/ADZP level of theory using the ADF 2017 software.^[18] All structures were optimized in presence of the COSMO implicit solvation model,^[19] using dielectric constant 15, a value consistent with those reported for similar ionic liquids.^[20] The species whose formulas (reported in Figure 4 and Table 1) are separated by a colon (:) were optimized together as an ionic (or neutral) pair, to capture part of the electrostatic stabilization, while those separated by a (+) sign were optimized separately. The thermal contributions to the free energies (zero-point energy and vibrational enthalpy and entropy)

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were neglected since they are expected to be very similar in all structures.

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Keywords: Ab initio calculations • aluminum secondary battery • energy storage • ionic liquids • polymer gel electrolytes

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Entry for the Table of Contents

Aluminum chloride and urea can form a deep eutectic solvent (DES) electrolyte for aluminum batteries. Adding polyethylene oxide (PEO) polymer turns the DES into a sticky and elastic gel which improves the battery's safety while retaining its electrochemical performance. The excellent mechanical properties are due to bonds formed between the PEO and the components of the DES, which can act as crosslinkers and contribute to the elastomeric character of the gel.

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