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Poly(glycidyl ether)s recycling from industrial waste and feasibility study of reuse as electrolytes in sodium-based batteries

Giulia Piana,^{1,†} Maria Ricciardi,^{2,†} Federico Bella,^{1,*,†} Raffaele Cucciniello,^{2,3,*} Antonio Proto,² Claudio Gerbaldi^{1,*}

1) *GAME Lab, Department of Applied Science and Technology - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 – Torino, Italy*

2) *Department of Chemistry and Biology “Adolfo Zambelli”, University of Salerno, Via Giovanni Paolo II 132, 84084 – Fisciano, Italy*

3) *MIUR - Ministero dell'Istruzione, dell'Università e della Ricerca, Viale Trastevere 76, 00153 – Roma, Italy*

† These authors contributed equally to the work

Corresponding authors: Federico Bella (federico.bella@polito.it, +39 0110904643), Raffaele Cucciniello (rcucciniello@unisa.it, +39 089969366), Claudio Gerbaldi (claudio.gerbaldi@polito.it, +39 0110904643).

Abstract: The need to recycle waste products, convert and reuse them for different high-value applications is a very up-to-date, utmost important topic. In this context, here we propose glycidol, a high-value product isolated from epichlorohydrin industry waste, as a starting material for the preparation of two poly(glycidol)s polymer matrices with a chemical structure mimicking that of poly(ethylene oxide), i.e. the most used polymer matrix for non-liquid battery electrolytes. The materials are characterized from the physico-chemical viewpoint, showing high thermal stability. They are then obtained in the form of ionic conducting polymer electrolytes encompassing different sodium salts and solvent mixtures. Ionic conductivity values exceeding 10^{-5} S cm⁻¹ are measured in the “dry” truly solid state at 80 °C, while it approaches 6×10^{-5} S cm⁻¹ at ambient temperature in the “wet” quasi-solid state. In addition, poly(glycidol)-based polymer matrices show reasonably wide electrochemical stability towards anodic oxidation. It envisages their possible use as separating electrolytes in secondary batteries, which is also demonstrated by preliminary charge/discharge cycling tests in lab-scale sodium cells. The present findings pave the way to a circular economy platform starting from industry wastes and ending with post-lithium storage systems.

Keywords: Poly(glycidyl ether); Waste recovery; Sodium battery; Polymer electrolyte; Circular economy.

1. Introduction

Since the industrial revolution, the rapid pace of technological progress has continued and, thanks to the resulting innovations, many people in our modern society make use of

products from all over the world at affordable prices, high-value products indeed absolutely unimaginable to previous generations. Unfortunately, this traditional linear economy based on a “take, make, dispose” production model is no more sustainable, and we clearly need to rethink and redesign the way we make things, recycling materials and, indeed, designing products that can be “made to be made again” and powering the system with renewable energy [1,2]. A new industrial model must be defined, which is based on a circular economy perspective, which entails a gradual but constant decoupling economic activity from the consumption of finite resources, and designing waste out of the system, thus aiming to redefine growth, and focusing on positive society-wide benefits [3,4]. This is indeed the best way to develop a thriving economy that can benefit everyone within the limits of our planet in terms of energy, eventually providing environmental and societal benefits on a long-term perspective [5].

Electrochemical energy storage systems have the potential to make a major contribution to the implementation of sustainable energy, being the solution of choice for many aspects of daily life, with a special focus on portable electronic devices and electric vehicles [6,7]. Indeed, batteries provide efficient, long lasting and reliable storage of electricity [8], particularly lithium-ion batteries (LIBs), which represent the most diffused technology thanks to their superior specific energy density, power and suitability for many applications (e.g., smartphones, notebooks, cars, etc.) [9]. However, the current LIB market is growing exponentially, up to an estimated value of 68 billion of dollars by 2022, and this makes the consumption of lithium one of the most worrying scenarios of the present days [10]. In this scenario, sodium-ion batteries (NIBs) represent a reliable and sustainable alternative, especially for large stationary storage plants [11,12], where record performances, weight and dimensions are not the most relevant aspects [13,14].

Commonly used electrolytes in NIBs are mainly based on solvents and polymeric separators taken/adapted from the LIB technology [15,16,17], by using sodium salts instead of the lithium counterparts [18,19,20]. Current state of the art electrolyte materials (liquid or polymer), such as fluoropolymers, carbonates, and complex polypropylene architectures, contribute to the high price of LIBs/NIBs and are made by energy consuming petrochemical industrial processes and oil refinery [21,22], generating pollution. This aspect should be carefully addressed by the scientific community, especially if the often-claimed eco-friendly aspects of sodium batteries are envisaged

[23]. In general, electrolytes can be liquid non-aqueous solvents entrapped in a non-woven separator, solid polymer (SPE) or gel-polymer (GPE) electrolytes, these latter based on solid polymers entrapping liquid electrolytes leading to quasi-solid systems with good ionic conductivity, which are also rather cheap to be prepared and less flammable, thus more safe [19,24]. Actually, these materials may be replaced by environmental friendly, green, biosourced materials, as already proposed by Subban *et al.* [25], Aziz *et al.* [26] and Colò *et al.* [27], which can, in addition, be obtained from recycling/reuse of industrial wastes.

In this scenario, the research of new bio-based polymers with potential application in energy storage devices, such as NIBs, might be of high interest for both industrial and research communities. A class of potential candidates for this purpose is represented by poly(glycidyl ether)s (PGs). PGs are sustainable and biodegradable polymers that can be obtained from glycidol (2,3-epoxy-1-propanol) and protected glycidol by controlled cross-linking and polymerization [28,29]. Recently, we demonstrated that glycidol can be obtained as high-value bio-based product from epichlorohydrin industry waste (Epicerol® process developed by Solvay) [30], and a detailed life cycle analysis (LCA) highlighted the sustainability of the entire process and all the environmental impacts [31]. Herein, considering an annual production of about 100 ktons of bio-based epichlorohydrin, 5 tons per year of glycidol can be obtained [32]. Glycidol is a very reactive molecule with several applications [33,34] and, therefore, the preparation of PGs from bio-glycidol might result definitely promising in the light of the twelve principles of Green Chemistry and circular economy perspective [35]. Structural similarities between PGs and PEO (the most widely used polymer matrix for SPEs and GPEs [36,37,38]) pushed us to formulate PGs-based gel polymer matrices having pendant ether groups that inhibit crystallization, this latter representing one of the major drawbacks for PEO at temperatures below 65 °C (often limiting its widespread practical application). In addition, PGs show beneficial characteristics, such as a large fraction of oxygen atoms able to promote salt dissociation and a low T_g useful to increase the ion mobility [39]. As a result, the polymer matrices demonstrated appreciably high ionic conductivity values when tested both in its “dry gel” form (with the addition of sodium salt) and “wet gel” form (by adding carbonate solvents), and reasonably high stability towards anodic oxidation, which postulates their possible

application as thermally stable electrolytes in NIBs, which was confirmed in the present work by the appreciable proof of operation in laboratory scale sodium-based cells.

2. Material and methods

2.1 Synthesis of polyethoxyethyl glycidyl ether (PEEGE) and polyglycidyl methyl ether (PGME)

Triisobutylaluminum ($i\text{Bu}_3\text{Al}$, 1 M in toluene) and *p*-toluenesulfonic acid monohydrate (98.5%) were purchased from Sigma-Aldrich and used as received. Tetraoctylammonium bromide (NOct_4Br , 98%) and ethyl vinyl ether (98%) were purchased from TCI Europe and used as received. Glycidyl methyl ether (GME, >85%, TCI Europe) and 2,3-epoxypropan-1-ol (glycidol, 96%, Sigma-Aldrich) were dried over CaH_2 and distilled under vacuum. Toluene was purified over polystyryllithium seeds and distilled under vacuum before use.

Ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol and ethyl vinyl ether in the presence of *p*-toluenesulfonic acid following the procedure described by Fitton and coworkers [40]. The as obtained EEGE was dried over CaH_2 and distilled under vacuum before use. Polymerization of EEGE was performed under inert (N_2) atmosphere in a glass reactor equipped with a magnetic stirrer. Initially, 64 mL of toluene and 12 mL of EEGE (78.8 mmol) were introduced in the polymerization reactor through connected glass tubes. Then, a 0.19 M solution of NOct_4Br in toluene (2.0 mL, 0.38 mmol) was added via a syringe under N_2 followed by the addition of 1.5 mL of a 1 M solution of $i\text{Bu}_3\text{Al}$ in toluene. The polymerization was allowed to proceed for 19 h at 0 °C, then stopped by addition of water and the solvent was removed under reduced pressure. Yield was determined gravimetrically after a complete drying of the polymer under vacuum at 50 °C.

PGME was synthesized in a glass reactor flamed under vacuum and cooled prior to the addition of 16 mL of toluene and 7 mL of GME (78.0 mmol) through connected glass tubes keeping the temperature at −30 °C. Then, a 0.14 M solution of NOct_4Br in toluene (1.6 mL, 0.23 mmol) was added via a syringe under N_2 followed by 1.6 mL of a 1 M solution of $i\text{Bu}_3\text{Al}$ in toluene and the reaction temperature was slowly raised up to 20 °C. After 7 h of reaction at 20 °C, the polymerization was stopped with addition of ethanol

and the solvent was removed under reduced pressure. Yield was determined gravimetrically after a complete drying of the polymer under vacuum at 50 °C.

2.2 Preparation of gel polymer electrolytes

Sodium bis(fluorosulfonyl)imide ($\text{NaN}(\text{SO}_2\text{F})_2$, NaFSI, 99.7%) and the electrolyte solution containing 1 M NaFSI in ethylene carbonate : diethyl carbonate (EC:DEC = 1:1 vol%), both battery grade, were purchased from Solvionic and used as received.

Gel polymer electrolyte matrices were prepared by mixing the gel polymer and the salt (“dry gel electrolyte”), or the gel polymer and the liquid electrolyte mixture (“wet gel electrolyte”), with different compositions (as detailed in **Table 1**). The process was carried out at 80 °C until a clear homogeneous viscous solution was obtained, in the inert atmosphere of a dry glove box (GP2 Concept by JACOMEX, O_2 and H_2O content < 1 ppm) filled with extra pure Ar 6.0, in order to prevent water contamination.

Table 1. Composition of “dry gel” and “wet gel” polymer electrolytes.

System	Polymer	M_w (g mol ⁻¹)	Content (wt%)	Salt	Content (wt%)	Solvent	Content (wt%)
PE-NaFSI	PEEGE	89 002	85	NaFSI	15	-	-
PG-NaFSI	PGME	46 265	85	NaFSI	15	-	-
PE-ECDEC	PEEGE	89 002	80	NaFSI	6 (1 M)	EC:DEC (1:1)	14
PG-ECDEC	PGME	46 265	80	NaFSI	6 (1 M)	EC:DEC (1:1)	14

2.3 Characterization techniques

Average molar masses of the synthesized polymers were determined by GPC at 25 °C using tetrahydrofuran as eluent with a flow rate of 1.0 mL min⁻¹ on a 150 C Waters apparatus equipped with a RI detector, a JASCO 875-UV (254 nm) detector and a set of four columns from PSS (pore size of 106, 105, 104, and 103 Å, particle size of 5 µm). Commercial polystyrene standards were used as reference for the calibration curve.

The ¹H and ¹³C NMR spectra of PEEGE and PGME were collected on Bruker Avance-400 [400(¹H) e 100(¹³C)] using CDCl₃ as solvent.

Thermogravimetric analyses (TGA) were carried out with a thermobalance (SDT Q600, TA Instruments) in the range 25-600 °C at 10 °C min⁻¹ heating rate under N₂ flow (100 cm³ min⁻¹ STP).

The ionic conductivity values were determined by electrochemical impedance spectroscopy (EIS) analysis of hermetic ECC-Std test cells by EL-CELL[®]. The cells were assembled by sandwiching the electrolyte sample between two stainless steel (SS-316) blocking electrodes, separated by a 120 μm thick Mylar[®] spacer with an internal diameter of 14 mm (area 1.54 cm^2), to keep the sample volume constant upon varying the testing temperatures. A VMP-300 potentiostat by Bio-Logic was used for measurements at various temperatures between 800 kHz and 1 Hz at the open circuit potential (OCV) with a sinusoidal applied potential equal to 20 mV. The Nyquist plot of the impedance led to determine the bulk resistance of the electrolyte, and the geometric cell constant was used to calculate the ionic conductivity. The temperature of the cell was controlled by a climatic chamber (UFE-400 Memmert GmbH, Germany).

Anodic stability window (ASW) was determined by linear sweep voltammetry (LSV) by means of a VMP-300 potentiostat by Bio-Logic. Each electrolyte sample was sandwiched between an Al foil and a Na metal disk, as working and counter electrodes, respectively, in the ECC-Std cell. A potential scan rate equal to 0.100 mV s^{-1} was fixed from the OCV to 5.5 V vs. Na^+/Na .

Galvanostatic discharge (Na^+ insertion)/charge (Na^+ deinsertion) cycling was conducted at 40 $^{\circ}\text{C}$ in ECC-Std test cells using an Arbin Instrument BT-2000 battery testing system. In a typical experiment, the electrolyte sample was sandwiched between a Na metal counter electrode and a TiO_2 -based working electrode, the latter being composed of a 74:8:18 ratio of commercial TiO_2 anatase (Hombikat), Na-CMC binder and conductive carbon, respectively, obtained by a water-based procedure. Again, the electrodes were separated by a 120 μm thick Mylar[®] foil with an internal diameter of 14 mm. The discharge/charge cycles were carried out at C/10 (cut off potentials: 0.2–3.0 V vs. Na^+/Na). To confirm the obtained results, tests were performed at least three times on different clean electrodes and fresh samples. Procedures of cell assembly were performed in the inert atmosphere of the dry glove box.

3. Results and Discussion

EEGE and GME were polymerized using a binary system composed by $i\text{-Bu}_3\text{Al}$ as catalyst and NOct_4Br as initiator, as firstly reported by Carlotti and co-workers for the anionic polymerization of protected form of glycidol, such as glycidyl ethers [41,42]. A

detailed scheme of the reaction pathway is shown in **Figure 1**, while details on the purification process and other experimental procedures were reported in our previous work [30]. The two desired polymers (PEEGE and PGME, see chemical structures in **Figure S1**) were obtained quantitatively and then characterized by NMR, GPC and TGA. ^1H NMR of PEEGE (400 MHz, CDCl_3): δ (ppm) 3.42-3.68 (m, 7 H, 1-2-3-6), 4.69 (q, 1 H, 4), 1.29 (d, 3 H, 5), 1.19 (t, 3 H, 7). ^{13}C NMR of PEEGE (400 MHz, CDCl_3): δ (ppm) 99.9 (C_4), 78.9 (C_2), 69.9 (C_3), 65.0 (C_1), 60.9 (C_6), 19.9 (C_5), 15.0 (C_7). ^1H NMR of PGME (400 MHz, CDCl_3): δ (ppm) 3.44-3.62 (m, 5 H, 1-2-3), 3.34 (s, 3 H, 4). ^{13}C NMR of PGME (400 MHz, CDCl_3): δ (ppm) 78.6 (C_2), 72.6 (C_3), 69.9 (C_1), 59.2 (C_4). NMR spectra are shown in **Figures S2-S5** in the Supporting Information.

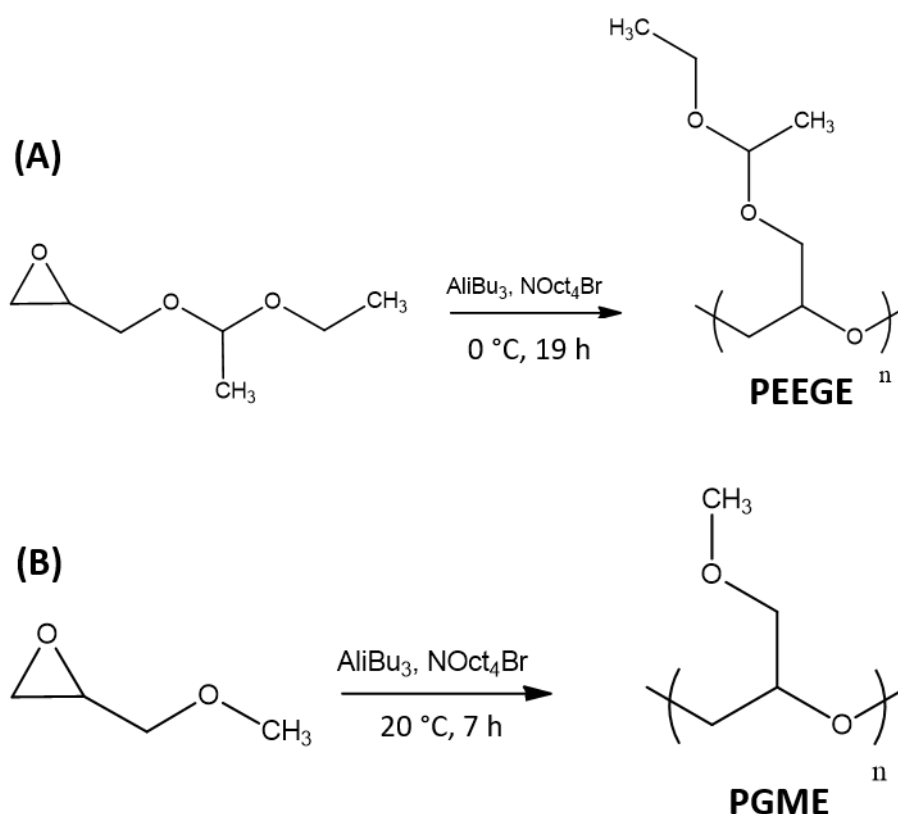


Figure 1. Reaction pathways to synthesize **A)** PEEGE and **B)** PGME polymers.

Experimental molar masses, determined by GPC based on a polystyrene calibration, were $M_n(\text{GPC}) = 83223\text{ Da}$ and $M_w(\text{GPC}) = 89002\text{ Da}$ with a PDI of 1.07 for PEEGE, $M_n(\text{GPC}) = 39860\text{ Da}$ and $M_w(\text{GPC}) = 46265\text{ Da}$ with a PDI of 1.16 for PGME.

TGA profiles of PEEGE and PGME polymeric gels are shown in **Figure 2**. The weight loss below 200 °C (about 2 and 5% for PEEGE and PGME, respectively) was attributed to moisture adsorbed during sampling or volatile organic impurities remained from preparation steps. The weight loss (40%) observed for PEEGE below 300 °C was related to the elimination of side groups [33,34]. The decomposition of polymer backbone chains occurred in the temperature range between 300 and 500 °C for both the polymers.

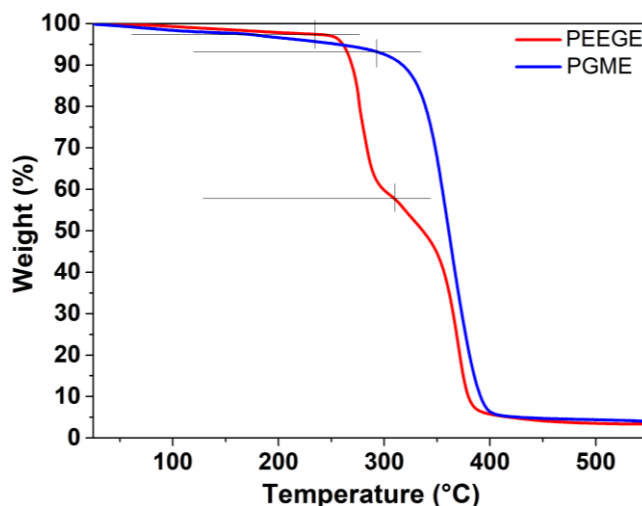


Figure 2. TGA profiles for PEEGE and PGME. The measurements were carried out under N₂ flow and at a scan rate equal to 10 °C min⁻¹.

Electrolytes obtained by addition of sodium salts to the previously described polymeric gels were homogeneous viscous fluids, which did not flow when the vessel was turned down and showed the typical behaviour of physical gels (see inset of **Figure 3**, representative for all the samples prepared in the “dry gel” form).

Ionic conductivity data for the “dry gel” electrolyte containing 15 wt% of sodium salts are shown in **Figure 3** in the temperature range between 20 and 80 °C. At 25 °C, PEEGE- and PGME-based electrolytes with NaFSI salt displayed an ionic conductivity of 3.2×10^{-7} and 3.9×10^{-7} S cm⁻¹, respectively. The slightly higher ambient temperature sodium ion conductivity of PGME compared to PEEGE is likely ascribable to its lower viscosity.

According to the literature [43,44], the ionic conductivity of classical PEO-based polymer electrolytes containing ≈ 18 wt% of NaFSI (i.e., EO:Na = 20) is in the order of $2\text{--}3 \times 10^{-7}$ S cm⁻¹ at 25 °C, which is similar to what obtained in this work with PGs-based systems. However, above the melting point at around 60 °C, the ionic conductivity of

PEO-based electrolytes increased significantly up to about $2.5 \times 10^{-4} \text{ S cm}^{-1}$ at 80°C . In our case, the polymeric gels did not melt in this temperature range (see **Figure S6** in the Supporting Information) and the ionic conductivity values at 80°C were limited to 2.9×10^{-5} and $1.9 \times 10^{-5} \text{ S cm}^{-1}$ for PE-NaFSI and PG-NaFSI electrolytes, respectively.

The plot shown in **Figure 3** highlights that the conductivity increased with the temperature by following the Arrhenius law:

$$\sigma = \sigma_0 \cdot e^{-\frac{E_a}{k_B T}}$$

where σ_0 is the conductivity pre-exponential factor and E_a is the activation energy for ionic conduction. Unlike standard PEO- or ionic liquid-based electrolytes, in the present case the evolution of the conductivity with temperature did not follow the Vogel-Tammann-Fulcher (VTF) equation. This could indicate that our polymeric gel electrolytes did not show relevant ionic interactions with sodium ions and did not take a leading role in the ionic transport (as typically occurs for systems where cations diffuse by the hopping mechanism between specific chemical moieties present in the polymer chains [45]). Activation energy (E_a) data represent an overall estimation of energy of defects formation and energy of defects migration within polymer electrolytes. The activation energy for PEEGE polymeric gel electrolyte with NaFSI was 0.33 eV, while activation energy was 0.29 eV for PG-NaFSI. This difference indicated that PGME polymer structure allows for more favorable ion transport compared to the PEEGE-based system.

When the electrolyte solution containing NaFSI 1.0 M in EC:DEC was added to the synthesized polymeric gels, the ionic conductivity increased by two orders of magnitude at ambient temperature, indicating that sodium ion conduction was facilitated by the solvation effect and the overall lower viscosity of the electrolyte. As expected by the addition of polar solvents, the activation energy of the system was considerably reduced upon the addition of 20 wt% of carbonate-based liquid mixture: PEEGE electrolyte activation energy decreased to 0.09 eV, while the PGME-based system showed an E_a value of 0.16 eV. **Table 2** summarizes experimental data and fitted parameters.

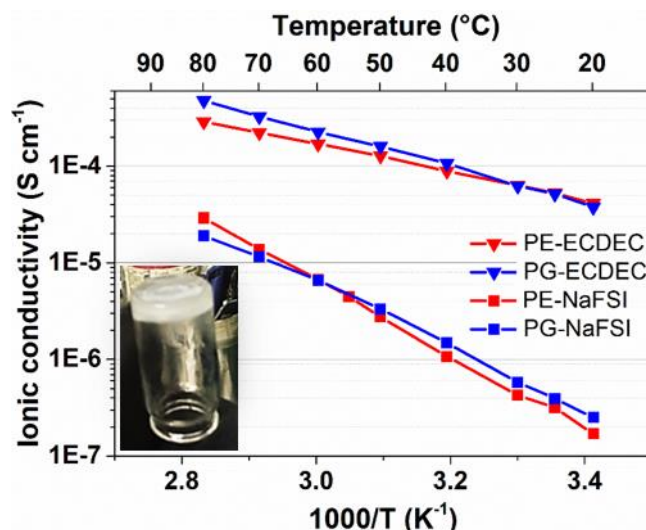


Figure 3. Arrhenius plots for the polymer electrolytes under study. PE-NaFSI and PG-NaFSI indicate “dry gel” polymer electrolytes containing NaFSI salt (free of solvents).

The inset shows a digital picture of PG-NaFSI sample, not flowing in a tilted vial.

Table 2. Ionic conductivity at 25 °C and fitted Arrhenius parameters for “dry gel” and “wet gel” electrolytes.

System	$\sigma_{25^\circ\text{C}}$ (S cm ⁻¹)	σ_0 (S cm ⁻¹)	E_a (eV)	R ²
PE-NaFSI	3.2×10^{-7}	289.4	0.31	0.992
PG-NaFSI	3.9×10^{-7}	111.7	0.29	0.997
PE-ECDEC	5.3×10^{-5}	0.4	0.09	0.991
PG-EDEC	5.2×10^{-5}	7.1	0.16	0.998

The electrochemical stability towards anodic oxidation was measured for PE-ECDEC and PG-ECDEC, samples laden with NaFSI salt, by performing a cyclic sweep voltammetry at 0.1 mV s⁻¹ at 25 °C (**Figure 4**). PE-ECDEC electrolyte was fairly stable up to 3.5 V *vs.* Na⁺/Na, while PG-ECDEC showed an enhanced stability towards oxidation up to 4.5 V *vs.* Na⁺/Na. We hypothesize that this difference between PG and PE systems lies in the chemical structure of the two polymers: methoxy groups in PG resulted more stable than the oxo (–O–C–O–) side chains moieties in PE polymer. This hypothesis fits well with previously published studies focused on methoxy groups-containing electrolytes [46].

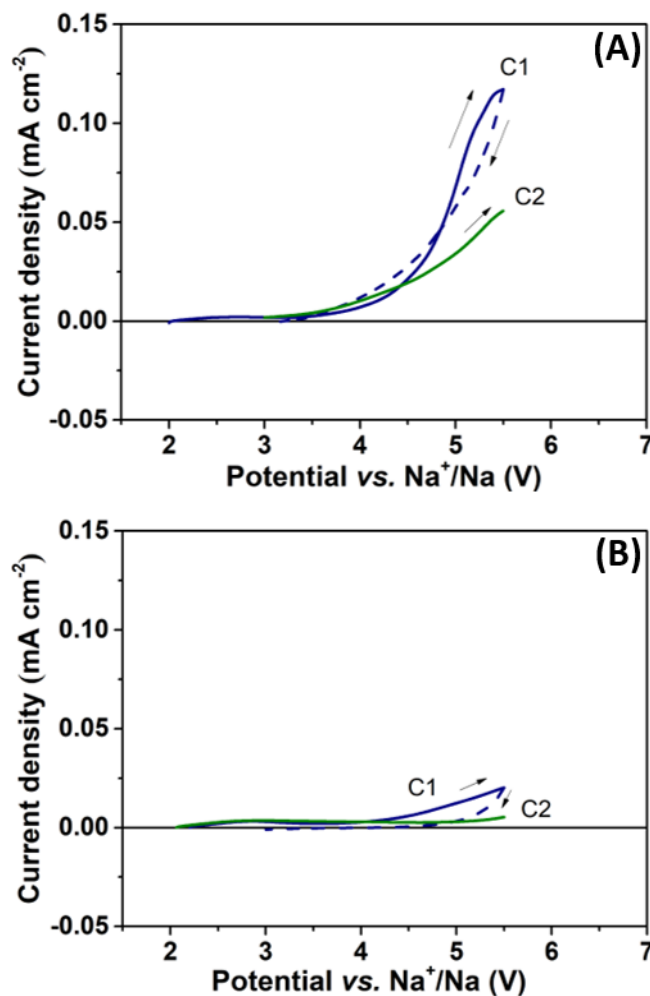


Figure 4. Anodic sweep voltammetry for PE-ECDEC (A) and PG-ECDEC (B) electrolytes, sandwiched between sodium and stainless steel electrodes. Experiments were carried out at 25 °C and 0.1 mV s⁻¹.

Sufficiently high ionic conductivity and anodic stability in the “wet gel” configuration postulate the practical use of the biosourced polymeric gels in secondary batteries. Thus, they were assembled in lab-scale cells with TiO₂ working electrode and Na metal counter and tested (galvanostatic charge/discharge cycling at 40 °C and C/10 current rate) for their feasibility as electrolytes in sodium-based batteries conceived for moderate temperature application. The relatively low (40 °C) temperature was chosen as the good compromise to avoid the evaporation of the embedded liquid solvent while concurrently being a suitable temperature for stationary NIBs applications.

Both the lab-scale TiO₂/Na cells with PE-ECDEC and PG-ECDEC polymeric gel electrolytes under study in this work showed the capability to reversibly operate at

moderate temperature. Representative performance and charge/discharge potential *vs.* specific capacity profiles of a few selected cycles extracted from the cycling tests are shown in panels A and B of **Figure 5AB** for PE-ECDEC and PG-ECDEC systems, respectively. In general, both the plots show clearly the characteristics sloped curves of sodium ion insertion/deinsertion into/from the anatase TiO₂ structure. More in details, the evolution of cell potential in the initial sodium ion insertion process (first discharge) is largely dominated by a steadily sloping pseudopotential plateau below 1.0 V *vs.* Na⁺/Na, and following almost straight plateau between 0.4 and 0.2 V, which accounts for an initial pronounced irreversible capacity and corresponding low Coulombic efficiency, well in agreement with recent studies [47]. This phenomenon was already observed by other research groups reporting about cycling of TiO₂ electrodes [48,49,50,51] and, although the mechanism is currently not fully understood, can be mainly ascribed to interfacial issues rather than decomposition or transport limitation in the electrolyte under study; indeed, it is often very difficult to stabilize the SEI layer in the presence of metallic sodium anodes [52,53]. This latter issue could be improved with the addition of specific additives in the electrolytes; being out of the scope of this work, for the sake of the readers we mention a couple of recent articles published to this purpose [9,54,55]. In the following cycles, the profiles changed gradually, and the materials stabilized their behavior showing the expected gradual evolution associated with a continuous solid-solution reaction between sodium ions and active material particles, following the progressive slight improvement of insertion/extraction of sodium ions into/from the bulk of the active material nanoparticles [56,57]. In addition, the polarization between charge and discharge profiles slightly decreases with the number of cycles, likely ascribable to a possible structure ordering driven by the reversible insertion of Na⁺ ions, along with some sort of interfacial contact enhancement and better wetting of the electrode structure by the polymeric gel electrolyte upon cycling. After the initial activation cycles, the specific capacity values remained almost constant until the end of the test: the specific capacity still amounts about 94 and 89 mAh g⁻¹ for PE-ECDEC and PG-ECDEC systems, respectively, indicating a reversible sodium ion uptake and release after 50 cycles.

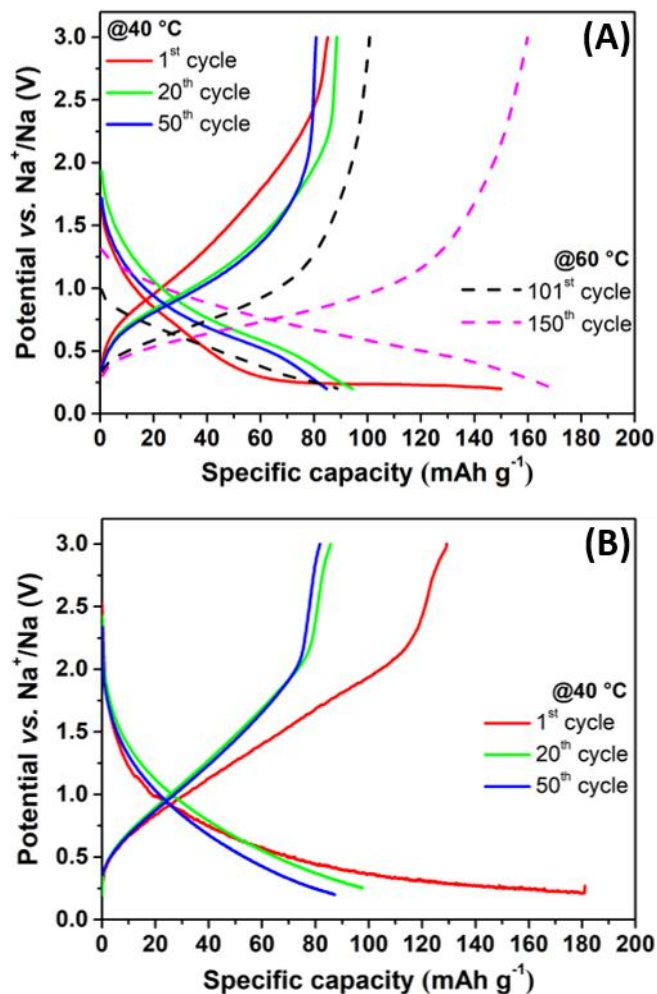


Figure 5. Cycling behavior of TiO₂/Na lab-scale cells assembled with PE-ECDEC and PG-ECDEC polymeric gel electrolytes at C/10 rate. **A)** Potential vs. specific charge/discharge capacity profiles of Na/PE-ECDEC/TiO₂; **B)** Na/PG-ECDEC/ TiO₂ cells.

In spite of the higher viscosity, PE-ECDEC-based cells showed slightly better cycling characteristics than PG-ECDEC counterparts in terms of capacity retention and stability with the number of cycles (in the former case, the charge capacity values remained almost constant from cycle 1 to 50). We may ascribe this result to the formation of a more stable passivating layer at the interface. At this stage, we are also performing charge/discharge experiments at 60 °C (**Figure 5A**) and an appreciable increase of specific capacity values is measured, maybe due to an improved wettability of the electrode; this latter, largely dependent on the viscosity of the electrolyte, is of primordial importance to control the TiO₂ active surface. An intensive work on device optimization is required and it will be

presented in a forthcoming paper. However, we actually demonstrated sufficient performance of the polymer gel electrolytes under study if one considers the values recently demonstrated with other polymeric systems, such as PEO/liquid crystals [58], PEO/poly(vinyl pyrrolidone) [59] and poly(vinylidene fluoride-co-hexafluoropropylene) [60], and that anatase TiO_2 electrode has a theoretical sodium ion capacity of 335 mAh g^{-1} and an experimental reversible initial capacity of $180\text{-}220 \text{ mAh g}^{-1}$ with liquid carbonate-based electrolytes at low current rates (lower than 1C) [48,61,62]. Noteworthy, the Coulombic efficiency finally exceeded 98% in all the tests, which is a reasonably high value considering the impact of the sodium metal counter electrode and interfacial contact with the polymeric gels on the overall cell efficiency.

Furthermore, we carried out EIS measurements of our cells just after assembly and at each hour for the subsequent 10 h. **Figure S7** in the Supporting Information shows the resulting Nyquist plot for the Na/PE-ECDEC/ TiO_2 cell at room temperature. Here, cell impedance increased in the first hours, accounting for the interfacial reactions, and then stabilizes after about 8 h.

4. Conclusions

In a circular economy perspective, biosourced poly(glycidyl ether)s derived from industrial byproducts have been here obtained in the form of polymeric gels, eventually characterized for their feasibility as suitable polymeric platforms for the preparation of electrolytes in electrochemical energy storage devices. The synthesis of PEEGE and PGME matrices was carried out and the resulting polymeric gels were characterized in terms of their physico-chemical properties, confirming high thermal stability and sufficient ionic conductivity values with different sodium salts or solvent mixtures, compatible with those typically required for battery electrolytes. In addition, the newly proposed electrolytes demonstrated rather wide electrochemical stability window (up to $>4 \text{ V}$), postulating their potential use in quasi-solid state batteries, as confirmed by preliminary feasibility study in terms of galvanostatic charge/discharge cycling in TiO_2/Na lab-scale cells, giving stable specific capacity values exceeding 80 mAh g^{-1} after 50 reversible cycles at 40°C and low current rate.

Considering the growing demand for high-performing, but sustainable and low-cost devices able to store the electricity produced from renewable sources, this work highlights

the possibility of designing battery components based on abundant materials (such as sodium) and sustainable or reused/recycled waste-derived components (such as PGs), therefore resulting in a step forward towards proofing the effective exploitation of the new chemistries and/or materials in the energy storage field.

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