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1 **Opening the door to liquid-free polymer electrolytes for** 2 **calcium batteries**

3

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15

16 **Abstract**

17 This work studies calcium-conducting, solvent-free polymer electrolytes in the
18 framework of today's post-lithium battery strategies. The samples consist of three
19 calcium salts: (i) Ca(CF₃SO₃)₂; (ii) Ca(TFSI)₂; and (iii) CaI₂ hosted by commercial
20 poly(oxyethylene) (POE). The data collected from X-ray diffraction (XRD), scanning
21 electron microscopy (SEM), differential scanning calorimetry (DSC) and
22 thermogravimetric analysis (TGA) indicate that the polymer electrolytes consist of stable
23 macromolecular solutions of these calcium salts. The polymer electrolytes yield
24 conductivities exceeding 0.1 mS·cm⁻¹; POE-Ca(CF₃SO₃)₂ reaching, at the moderate
25 concentration O/Ca =30, a conductivity of 0.47 mS·cm⁻¹. This preliminary and

1 fundamental study, which demonstrates the stability of Ca-conducting polymer
2 electrolytes, paves the way to the development of improved polymer electrolytes based
3 on oxyethylene repeat units and new calcium salts.

4
5 **Keywords:** Calcium electrolytes; calcium batteries, polymer electrolytes; energy storage;
6 poly(oxyethylene), (POE, PEO).

7 8 **1. Introduction**

9 The market for batteries, which approached 50 billion \$ in 2012 [1], is expected to grow
10 by more than 60% by 2020; such a growth is expected to reach 100% in the case of lithium
11 batteries (LiBs). Long-time confined to portable electronics, the growth of the market for
12 LiBs is driven by those developments achieved in Battery Electric Vehicles (BEVs) and
13 Plug-in-Hybrid Electric Vehicles (PHEVs). The latter are expected to play a crucial role
14 to curtail both greenhouse gas emissions and urban pollution. Indeed, as concerns the
15 automotive market, the Federal Council of Germany voted to ban internal combustion
16 engines (ICEs) by 2030 [2], while in France the ban on ICEs has been placed by 2040
17 [3]. These decisions are yielding a huge impact on the development strategies of car
18 manufacturers, greatly promoting the diffusion of BEVs and PHEVs. Besides BEV and
19 PHEV, non-mobile grid-levelling applications typically require large-scale energy
20 storage systems to buffer the intermittency of the demand and, in the case of renewable
21 energies such as solar and wind, of the supply of electricity. However, the high cost of
22 LiBs bottlenecks their application as large-scale energy storage systems for the power
23 grid [4]. Hence, the end users require cheaper, safer and more efficient batteries for both
24 electric vehicles and stationary energy storage applications. Such criteria often contradict
25 one another. More efficient: if the electrode materials were changed from

1 $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$ to C/LiCoO_2 , the battery energy density would increase from 70 to
2 $200 \text{ Wh}\cdot\text{kg}^{-1}$; however, at the same time, the cyclability of the device would be reduced
3 [5]. Safer: regarding safety, the combustion of a 18650 Li-ion cells releases twice the
4 energy of a TNT grenade by summing the cell energy ca. $0.93 \text{ J}\cdot\text{g}^{-1}$ and the combustion
5 energy of organic components i.e. solvents, separator and binders [6]. Cheaper: even if
6 the cost of battery packs is constantly decreasing [7], the target of $150 \text{ \$}\cdot\text{kWh}^{-1}$ has not
7 been reached yet owing to the material costs and to the processing cost of LiBs [8,[9].
8 Another handicap suffered by LiBs in the medium term is the shortage of lithium ores,
9 triggered by the huge demand for this energy storage technology. Thus, it is mandatory
10 to devise new batteries where Li is replaced by cheaper elements that are more abundant
11 in Earth's crust, *e.g.*, Na, K, Mg and Ca, whose properties are compared in Table 1.

12 The ideal solution to devise high-energy density batteries remains based on the
13 implementation of metals at the negative electrode. This approach yields important
14 advantages, as it raises the capacity, the voltage and the energy density of the battery;
15 concurrently, the processing of the battery is simplified and the ohmic losses are reduced.
16 It should be highlighted that calcium and lithium exhibit the same volumetric capacity.
17 Furthermore, calcium is characterized by a very low reduction potential, -2.87 V vs. SHE ,
18 close to lithium one (-3.05 V vs. SHE). In addition, calcium exhibits the highest electrical
19 conductivity among the metals listed in Table 1. On the other hand, one relevant
20 parameter for the battery safety is the melting temperature of the alkaline/alkaline-earth
21 metal anode. Calcium melts at 842°C ; this is the highest melting temperature among all
22 the metals listed in Table 1. Hence, it is inferred that a battery based on a calcium metal
23 negative, Ca^0 , would provide high capacity and high safety as compared to a graphite
24 electrode, which barely exhibits a reversible capacity of 85 mAhg over 200 cycles and
25 co-intercalates solvent molecules as DMAC [10]. Based on all these pieces of

1 information, a Ca^0 -based calcium battery, CaB, would be a perfect post-lithium
2 alternative. A non-rechargeable CaB, was early proposed by Peled *et al.* [11][12][13], who
3 claimed similar performances than LiB ones and improved safety, but did not succeed in
4 cycling Ca^0 . More recently, a 600 mAh/g practical capacity was reported for a Ca^0/S
5 primary CaB [14]. Regarding the cycling issue of Ca^0 , Aurbach *et al.* [15] reported the
6 first general study concerning Ca^0 behavior in aprotic organic liquid electrolytes based
7 on $\text{Ca}(\text{ClO}_4)_2$ where, contrary to Li^0 , Ca^{2+} deposition onto Ca^0 did not occur. Post-mortem
8 analyses of the Ca^0 surface revealed the presence of passivation films of $\text{Ca}(\text{CO}_3)_2$ and
9 $\text{Ca}(\text{OH})_2$, which prevent further diffusion of Ca^{2+} and its deposition on Ca^0 . For a long
10 time, the deposition of Ca^{2+} onto Ca^0 , only occurred at very high temperatures [16][17].
11 The contribution of Ponrouch *et al.* [18] shows promise results, as it demonstrates the
12 deposition at temperatures in the range of 75-100 °C of Ca^{2+} onto Ca^0 from a liquid
13 electrolyte based on cyclic carbonates. However, this deposition process, observed from
14 cyclic voltammetry measurements, was characterized by a high overpotential and a low
15 capacity. In view of the observed passivation of Ca^0 by $\text{Ca}(\text{CO}_3)_2$ [15], the selected cyclic
16 carbonates are probably not the most suitable solvents for this application. P.G. Bruce *et*
17 *al.* [19] recently reported improved calcium deposition/stripping, discarding cyclic and
18 acyclic carbonates but using, as electrolyte, a THF solution of $\text{Ca}(\text{BH}_4)_2$. In this case,
19 deposition/stripping was observed at room temperature, over 50 cycles with a much lower
20 polarization and a better plating/stripping than those reported by Ponrouch [18]. The
21 formation of CaH_2 , which derives from the dehydrogenation of THF into 2,3-dihydrofuran,
22 was observed on Ca^0 . As stated by the authors and pointed out by Ponrouch [20], the
23 electrolyte used in this work exhibits too low anodic stability to be used with a high-
24 potential cathode and the THF solvent undergoes a significant degradation. Therefore,
25 neither carbonates nor THF could allow cycling efficiently calcium batteries. Besides, the

1 review of Muldoon *et al.* [21] ascribed the lack of interest for CaB to the lack of suitable
2 electrolytes. Can calcium polymer electrolytes, CAPE, become an alternative to liquid
3 ones? First results evidenced fairly high conductivities of Ca salts hosted by solvent-free
4 commercial poly(oxyethylene) POE or *PEO* homopolymer and POE-based amorphous
5 networks [22]. It has been recently reported that highly concentrated polymeric solution
6 of calcium nitrate in poly(oxyethylene) and poly(oxytetramethylene) networks, both
7 obtained by UV insolation [23][24] can provide at high temperature (110°C) conductivities
8 in excess of 0.1 mS/cm. Regarding CAPE, high conductivity is a necessary but not
9 sufficient condition: it is indeed essential to form stable macromolecular solutions of Ca
10 salts in a wide range of salt concentrations. As a matter of fact, polypropylene oxide, PPO,
11 long time used as an amorphous alternative to POE regarding Infra-Red and Raman
12 studies, was found, a decade later, to undergo microphase separation with several POP/Li
13 salts electrolytes [25]. In this work, we aim at investigating solvent-free polymer
14 electrolytes to pave the way towards the development of sustainable and cheaper batteries
15 with improved safety. As a first approach, we study the features of polymer electrolytes
16 based on a “reference” host polymer, *i.e.*, poly(oxyethylene), POE or PEO, hosting
17 different Ca salts.

18

19 **2. Experimental**

20 **2.1. Materials**

21 Analytical-grade reagents were supplied by Sigma-Aldrich. Poly(oxyethylene) (POE)
22 (M_w $3 \cdot 10^5$ g·mol⁻¹) was used as the host polymer. In a first approach, calcium
23 trifluoromethane sulfonate, Ca(CF₃SO₃)₂, was used to prepare polymer electrolytes at
24 different O/Ca ratios (8, 16, 20, 30, 40). For comparison purposes, calcium polymer
25 electrolytes based on calcium iodide, CaI₂, and calcium

1 bis(trifluoromethanesulfonyl)imide, $\text{Ca}(\text{TFSI})_2$ were also prepared at two O/Ca ratios (30
2 and 40).

3

4 **2.2. Preparation of POE-based electrolytes**

5 The green approach previously described [26] is applied to obtain electrolyte films.

6 Briefly, each electrolyte film is obtained by dissolving in deionized water specific
7 amounts of POE and the corresponding calcium salt according to the O/Ca ratios. For
8 instance, in case of the POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ electrolyte (O/Ca=40), 0.19 g of $\text{Ca}(\text{CF}_3\text{SO}_3)_2$
9 were dissolved in 1g of POE and 10 ml of deionized water. Solutions are stirred for five
10 hours, frozen at -20°C and then lyophilized over the course of 48 hours by means of a
11 FreeZone instrument (LABCONCO, USA). The resulting powders are then deposited on
12 a stainless steel plate and brought to 100°C for 20 minutes; this process: (i) eliminates
13 the residual moisture; and (ii) melts the powders. The melted polymer undergoes hot-
14 pressing at 50 kN and 100°C , resulting in films that exhibit a thickness of 100-150 μm .
15 Films obtained are further dried under vacuum at 50°C for 12 h and stored in a glove box
16 (M. Braun, GmbH, Germany) filled with argon, in which moisture was lower than 1 ppm
17 to prevent any water absorption.

18

19 **2.3. X-Ray diffraction**

20 X-Ray diffraction (XRD) measurements were carried out using a Philips X'PERT MPD
21 diffractometer ($\text{Cu K}\alpha$ radiation) operating at 40 kV and 40 mA. The XRD patterns were
22 recorded over a 2θ range of $5-80^\circ$ using a step scan of 0.02° and a counting time of 1 sec
23 per step.

24

25 **2.4. Scanning Electron Microscopy (SEM)**

1 The distribution of calcium in the electrolytes was studied by using the FEI Teneo
2 Scanning Electron Microscope. For this purpose, X-ray mapping involving the creation
3 of multiple elemental maps was performed at 6 kV and 0.8 nA using the EDAX TEAM™
4 EDS Analysis System for samples based on Ca(CF₃SO₃)₂, CaI₂ and Ca(TFSI)₂, all at
5 O/Ca=30.

6

7 **2.5. Thermal and thermomechanical analyses**

8 The thermogravimetric analysis (TGA) of samples (~8.5 mg) was performed using a Pyris
9 1 TGA (Perkin Elmer, USA) thermogravimetric analyzer. Samples were heated in a
10 platinum crucible from 30°C to 650°C (at 10°C·min⁻¹) under a nitrogen atmosphere. The
11 onset temperature (T_{onset}) was established as the intersection point between the tangent
12 drawn at the point of highest slope with the extrapolated baseline. Differential scanning
13 calorimetry (DSC) was conducted using a DSC822e (Mettler Toledo, Switzerland) under
14 a 50 mL·min⁻¹ constant flow of nitrogen. The melting temperature (T_m) and the enthalpy
15 of fusion (ΔH_m) were estimated between -90°C and 150°C (scan rate: 10°C·min⁻¹). DSC
16 measurements were collected during the second heating scan; the first heating scan
17 removes the thermal history of the samples. The relative percentage of crystallinity (X_c)
18 was directly related to the area under the 1st melting peak by using equation 1 [27]:

19

$$20 \quad X_c = \Delta H_m / \Delta H_m^0 \times 100\% \quad (\text{eq. 1})$$

21

22 where ΔH_m is the melting enthalpy estimated experimentally and ΔH_m⁰ is the melting
23 enthalpy for 100% crystalline POE (213.7 J·g⁻¹ [28]). Dynamic Mechanical Thermal
24 Analyses (DMTA) were carried out using a DMA Q800 machine (TA Instruments, USA)
25 working in tensile mode at 1 Hz and at an oscillation amplitude of 15 μm. DMTA samples

1 were rectangular (2.5 mm x 7.5 mm), with a thickness ranging between 100 and 150 μm .
2 DMTA measurements were performed by heating samples from -100°C to $+120^{\circ}\text{C}$ at a
3 heating rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$ in air atmosphere.

4

5 **2.6. Ionic conductivity measurements**

6 Conductivity measurements are collected by Impedance Spectroscopy (IS) using an
7 Impedance/Gain-Phase Analyzer SII1260 (Solartron, UK) and applying a 100 mV
8 amplitude signal in the 1 Hz - 10 MHz frequency range. The measurements were carried
9 out upon heating, at temperatures between 20 and 90°C with a step of 10°C . The samples
10 are sandwiched between stainless steel blocking electrodes ($\varnothing = 11$ mm) embedded in a
11 Swagelok-Nylon cell. A dwell time of 30 minutes between measurements was found to
12 be enough for the system to reach a stable temperature.

13

14 **3. Results and Discussion**

15 Since high molecular weight POEs undergo dramatic chain breaking even as its solutions
16 are mildly sheared [29], we chose the commercial grade having a molecular weight of
17 300,000 $\text{g}\cdot\text{mol}^{-1}$. Among the calcium salts previously used in liquid electrolytes can be
18 quoted $\text{Ca}(\text{ClO}_4)_2$ [15], $\text{Ca}(\text{CF}_3\text{SO}_3)_2$, $\text{Ca}(\text{BF}_4)_2$ [18][19]. We discarded $\text{Ca}(\text{ClO}_4)_2$ for
19 safety reasons and $\text{Ca}(\text{BH}_4)_2$ because both its limited anodic stability and its expected too
20 low conductivities in non-polar CAPE. As for $\text{Ca}(\text{BF}_4)_2$ we feared the possible
21 disproportionation of the tetrafluoroborate anion into BF_3 and F^- leading to a highly
22 resistive SEI made of CaF_2 . For the same reasons we didn't pay attention to PF_6^- and FSI
23 $[(\text{F}-\text{SO}_2)_2]^-$ anions still more likely than BF_4^- to generate CaF_2 . Even though C-F bonds
24 can be broken in contact with highly reductive metals as alkaline ones via metal-halogen
25 exchange, we assumed that this reaction would be more limited in aprotic solvent-free

1 polyether and selected calcium triflate and calcium trifluoromethane sulfonyl imide, both
2 anions exhibiting a high anodic stability. Due to its intrinsic stability in reduction, the
3 third salt, CaI₂, has been selected despite its limited anodic stability ($E_0 = 0.54$ V vs. SHE).

4 **3.1. Microstructural analysis**

5 A thorough characterization by XRD and DSC of POE-Ca(CF₃SO₃)₂ salt complexes was
6 previously reported by Mehta *et al.* [31]. XRD was used to characterize crystallinity
7 variations in the POE-Ca(CF₃SO₃)₂ polymer electrolytes as related to the concentration
8 of salt. XRD patterns of: (i) pristine, “*salt-free*” POE; (ii) samples with different O/Ca
9 ratios; and (iii) Ca(CF₃SO₃)₂ salt are reported in Figure S1 of Supplementary Information.

10
11 The homogeneous distribution of calcium in the polymer electrolytes was evaluated by
12 X-ray mapping at room temperature. Three samples with the same salt concentration
13 (O/Ca=30) were investigated, each including a different calcium salt. According to Figure
14 1, the X-ray mapping does not reveal any heterogeneity in the distribution of calcium, nor
15 the presence of pores. This confirms that the proposed lyophilization/hot-pressing
16 preparation procedure is able to yield highly homogeneous samples.

17 18 **3.2. Differential scanning calorimetry (DSC)**

19 DSC measurements were performed to elucidate the microstructural variations of the
20 polymer electrolytes as related to the salt concentration and type. In general, the
21 endothermic peaks shown in Figure 2, corresponding to melting temperature T_m , shift to
22 lower temperatures as the concentration of salt raises. The shift of T_m to lower
23 temperatures as the concentration of salt increases is associated to the more amorphous
24 microstructure induced by the polymer/salt interactions. Table 2 summarizes T_m , melting
25 enthalpy (ΔH_m) and crystallinity (X_c) for all calcium polymer electrolytes at different

1 O/Ca ratios. ΔH_m , decreases as the salt concentration raises. In agreement with XRD, this
2 evidence is consistent with a reduction in the degree of crystallinity.

3 It can be noticed that T_m and X_c of POE-Ca(CF₃SO₃)₂ (O/Ca=20) are lower than those
4 reported for the analogue Na-based polymer electrolytes (*i.e.*, POE-NaCF₃SO₃ with
5 O/Na=20) [26]. Such variation could be ascribed to the features of the salts. On one hand,
6 the size of Ca²⁺ and Na⁺ cations (coordination number: 6) are comparable (1.14 vs 1.13
7 Å from fluorides; 1 vs 0.99 Å from oxides). On the other hand, Ca²⁺ is divalent. Thus,
8 with respect to Na⁺, Ca²⁺: (i) is more likely to undergo interchain cross-solvation; and (ii)
9 is associated to two monovalent CF₃SO₃⁻ anions instead of only one. Indeed, CF₃SO₃⁻ are
10 expected to provide an important contribution to modify the microstructure of the
11 polymer electrolyte, facilitating the segmental mobility of the POE macromolecules.

12 Regarding the effect of the anions of calcium salts, the lowest crystallinity was obtained
13 for POE-Ca(TFSI)₂ polymer electrolytes. It is also highlighted that the difference in
14 crystallinity between POE-Ca(TFSI)₂ and POE-Ca(CF₃SO₃)₂ is markedly lower than that
15 observed between POE-LiTFSI and POE-LiCF₃SO₃ [32]. Moreover, T_m values are
16 slightly higher for POE-Ca(TFSI)₂ electrolytes. Hence, it is inferred that the main effects
17 influencing the microstructure of POE arise from: (i) the interactions between Ca²⁺ and
18 the POE chains; and (ii) the hindering resulting from Ca²⁺ bivalence (2 anions by cation).

19 Since the proposed POE-based calcium polymer electrolytes are semi-crystalline, DSC is
20 unable to estimate accurately the glass transition temperature, T_g . Indeed, in these
21 materials the crystalline phase constrains the amorphous phase, providing an “*artificial*”
22 T_g that is not accurate and is not reported in Table 2. Such a limitation could be addressed
23 by supercooling the semi-crystalline polymer electrolyte, quenching the melted
24 electrolyte at a very high speed would impede crystallization processes. However, this is
25 usually not possible with most commercial DSC equipment. The DSC analyses carried

1 out on the proposed POE-based polymer electrolytes from room temperature to 300°C
2 reveal the presence of an endothermic peak with an onset at 270°C and a maximum at
3 287°C. In accordance with the results obtained by Metha *et al.* [31], this peak is ascribed
4 to the precipitation of calcium salts out of the liquid polymer electrolyte owing to the
5 negative entropy of dissolution of calcium triflate in POE. This precipitation does not
6 affect the applicability of the proposed calcium polymer electrolytes as it occurs at
7 temperatures that are much higher than the typical operating temperatures of these
8 systems ($T < 100^\circ\text{C}$).

9

10 **3.3. Thermogravimetric analysis (TGA)**

11 Table 3 lists the onset temperatures of: (i) initial weight loss; (ii) residue at 450°C; and
12 (iii) percent (%) of non-volatile residues as compared to the wt% of salts in the various
13 POE-based polymer electrolytes.

14 The POE host was completely removed as temperature raised above *ca.* 400°C. Hence,
15 the residues detected at higher temperatures can be correlated to the other components
16 included in the POE-based polymer electrolytes, namely the CaX_2 salts. Thus, comparing
17 the residues at 450°C (roughly the onset of a thermal degradation plateau) with the
18 nominal content of CaX_2 in the polymer electrolytes, it can be deduced that both CaI_2 and
19 $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ are not significantly affected, while most of $\text{Ca}(\text{TFSI})_2$ undergoes
20 degradation. The POE- CaI_2 polymer electrolytes exhibit the lowest $T_{\text{onset}} \sim 350^\circ\text{C}$. This
21 evidence is ascribed to the reaction between the degradation byproducts of POE and CaI_2 ,
22 which releases I_2 . The latter is easily removed, as it already undergoes sublimation at
23 room temperature and is characterized by a boiling point (B_p) equal to 183°C. Since POE-
24 CaI_2 polymer electrolytes do not lose weight below 350°C, I_2 is not produced in the

1 operating temperature range of solvent-free batteries. Accordingly, CaI_2 is applicable in
2 Ca polymer electrolytes.

3 With respect to the pristine POE host, the introduction of CaX_2 salts raises the temperature
4 of the weight loss by *ca.* 100°C . This does not mean that thermal degradation is delayed
5 by the presence of the CaX_2 salts, but rather that the volatile degradation byproducts
6 interact with Ca salts, increasing their volatilization temperature [26]. It is worth to
7 highlight that TGA analyses discussed so far were carried out under an inert atmosphere.
8 These conditions reflect neither the real atmosphere in a battery, nor the conditions after
9 its failure. Furthermore, scanning experiments such as those discussed so far do not allow
10 achieving reliable information on how the weight loss at a given temperature depends on
11 time. To address these issues, isothermal studies were carried out in the presence of
12 oxygen. Figure 3 displays the weight losses of $\text{POE-Ca}(\text{CF}_3\text{SO}_2)_2$ at 100°C and 170°C . It
13 is shown that the onset of the thermal degradation occurs at much lower temperatures
14 than those listed in Table 3. A negligible weight loss of less than 0.5% was noticed at
15 100°C . With this thermal stability, $\text{POE-Ca}(\text{CF}_3\text{SO}_2)_2$ and most likely also the other POE-
16 CaX_2 polymer electrolytes can be used in a battery operating at temperatures at least as
17 high as 100°C . On the other hand, Table 3 reveals that these polymer electrolytes are
18 thermally unstable at 170°C since they exhibit an average weight loss of 2.8% per hour.
19 Indeed, in the case of an exothermal event, the temperature of the battery can reach and
20 even exceed 170°C . It is emphasized that in the first hour at $T = 170^\circ\text{C}$ only 0.9% of
21 volatile, thus easily flammable byproducts are released. This is not an absolute safety
22 guarantee, but must be compared to the low Flash Point (F_p) of liquid electrolytes used in
23 conventional lithium batteries. One example is dimethyl carbonate, DMC, whose F_p is
24 approximately $\sim 17^\circ\text{C}$.

25

1

2 **3.4. Thermomechanical behavior of POE-Ca(CF₃SO₃)₂ electrolytes**

3 The mechanical properties of POE-Ca(CF₃SO₃)₂ electrolytes were studied by DMTA as
4 a function of the temperature and of the concentration of dissolved Ca(CF₃SO₃)₂. Figure
5 4 shows the storage modulus (E') as a function of the temperature for samples with
6 different O/Ca ratios.

7 In the vitreous state, E' ranges between 4.4 and 5.1 GPa. In accordance with the
8 concentration of Ca(CF₃SO₃)₂, E' decreases as the salt concentration raises, since a
9 decrease in crystallinity is produced, as previously stated through the DSC analysis.

10 The glass-rubber transition is marked by: (i) a clear drop of the storage modulus; and (ii)
11 a peak in the tan δ signal, whose maximum is associated to the nominal glass transition
12 temperature, T_α, reflecting the segmental mobility of the polymer electrolytes. Since T_g
13 values measured from DSC are artificially increased by the constraining caused by the
14 crystalline regions, they are investigated by DMTA on samples that had not undergone
15 any thermal treatment and, accordingly, were in their pristine state. In general, T_α values
16 are significantly higher than the T_g measured by DSC. A similar evidence, consisting of
17 a gap of *ca.* 15°C between T_α and T_g, was recently observed on poly(oxyethylene)
18 networks having much lower crystallinity and T_m [33] than the POE homopolymer.

19 For samples reported in Figure 4, T_α values slightly shift to higher temperatures (up to ~
20 10°C), whereas the tan δ peak becomes gradually higher and broader as the salt
21 concentration increases. In semi-crystalline polymers the behavior of tan δ illustrates only
22 the segmental dynamics of the amorphous regions. Thus, it is generally observed that the
23 amplitude of tan δ evolves, becoming sharper and more intense, as the crystallinity degree
24 decreases. Thus, the tan δ behavior revealed by the POE-Ca(CF₃SO₃)₂ polymer
25 electrolytes may arise from the fact that the decrease of crystallinity, which normally

1 facilitates the increase of the segmental mobility when the salt is less diluted, may be
2 counterbalanced by stronger interactions between the salt and the polymeric
3 macromolecular solvent. Since the mechanical strength is mainly dependent on the
4 crystalline phase, the storage modulus drops dramatically above the melting temperature,
5 leading to creeping phenomena as $T \geq 80^\circ\text{C}$. The evolution of E' was studied up to 100°C
6 to reveal possible transient crosslinking triggered by the divalent nature of the cations and
7 ascribable to Ca^{2+} interchain solvation. For that purpose, POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ and POE-
8 $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ samples with different salt concentrations were compared. Although in the
9 range of uncertainties, two trends can be highlighted. First, for both alkaline-earth based
10 POE electrolytes, creeping decreases as the salt concentration lowers. For all salt
11 concentrations, the resistance to creeping of POE- $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ is higher than that of
12 POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$. This is in agreement with the higher hardness (HSAB theory) of Mg
13 vs Ca and also with the mechanical strength improvement induced by stronger
14 magnesium-oxygen bonds (Mg-O) [34]. However, despite the divalent nature of Ca^{2+} and
15 Mg^{2+} , this resistance to creeping is not as high as that previously observed for POE-
16 NaCF_3SO_3 ($\text{O}/\text{Na} = 20$). Indeed, in that case, E' reached values up to 98 MPa at 80°C
17 [26]. Even though the mechanical analyses only provide macroscopic descriptions of a
18 given material, one can assume that if both Ca^{2+} and Mg^{2+} benefit from interchain and
19 intrachain solvation, the latter is not predominant. Moreover, early studies [35][36] dealt
20 with a POE complex including HgCl_2 . In such systems, Hg^{2+} was located in a POE helix,
21 highlighting that solvation by POE of divalent cations may lead to a complex amorphous
22 phase dynamic.

23

24 **3.5. Ionic conductivity**

1 The conductivity studies were carried out by Electrochemical Impedance Spectroscopy
2 (EIS) in the frequency and temperature range of 1 Hz – 10 MHz and 20 – 90°C,
3 respectively. The profile of the real component of the complex conductivity (σ') as a
4 function of frequency and temperature, for three selected compositions based on
5 $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ is shown in Figure 5.

6 The profile of the real component of conductivity presents a plateau, corresponding to the
7 global ionic conductivity, which shifts to higher values as temperature increases and to
8 higher frequency as the O/Ca ratio increases.

9 The trend of global ionic conductivity as a function of temperature and salt concentration
10 during heating for samples based on $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ is reported in Figure 6.

11 At 20°C, all POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ samples exhibit a very low conductivity, in agreement
12 with the semi-crystalline nature of the polymer electrolyte. The ionic conductivity
13 increases as the temperature raises for all O/Ca ratios. Conductivity maxima were reached
14 at 90°C and ranged from $0.23 \text{ mS}\cdot\text{cm}^{-1}$ (O/Ca=8) to $0.47 \text{ mS}\cdot\text{cm}^{-1}$ (O/Ca=30 very close
15 to O/Ca =40). In this sense, it must be emphasized that, with respect to POE- LiCF_3SO_3
16 electrolytes, the ionic conductivity of POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ electrolytes is significantly
17 higher [37]. In both liquid and polymer electrolytes, the conductivity depends on both the
18 salt concentration and the mobility of the ions. As the concentration of salt in the
19 electrolyte raises, the concentration of mobile ions is globally increased; at the same time,
20 the ion pair dissociation and the mobility of the ions is decreased; consequently, the
21 viscosity of liquid electrolytes raises and the segmental motion in solvent-free polymer
22 electrolytes is inhibited. As a result of these opposite phenomena, in both liquid and
23 polymer electrolytes, the ionic conductivity reaches a maximum at a specific
24 concentration of salt. The highly concentrated sample characterized by an O/Ca ratio of
25 8 creeps at high temperature. On the other hand, from the conductivity plots it can be

1 assumed that the other compositions do not creep in the explored temperature range.
2 Therefore, the highest conductivity (that reached $0.47 \text{ mS}\cdot\text{cm}^{-1}$), was obtained for the
3 concentrations of $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ corresponding to $\text{O}/\text{Ca} = 30$, even though the gap with the
4 lowest one i.e. $\text{O}/\text{Ca} = 8$ barely exceeds a factor 2. Nonetheless, as the Ca^{2+} charge is
5 twice that of Li^+ , these concentrations are comparable to those corresponding to a $\text{O}/\text{Li} =$
6 15 or 4, while the practical salt concentrations in Li-polymer batteries range between 20
7 and 30. As compared to the conductivities reported for the CAPEs based on poly(PEG-
8 di-acrylate) network and calcium nitrate [24], our CAPE of concentration $\text{O}/\text{Ca} = 30$ leads,
9 at 90°C , to conductivity values roughly ten times higher than those obtained for Li-PE
10 with an equivalent O/Li ratio. This can be ascribed both to the higher dissociation of Ca
11 triflate compared to Ca nitrate and to the high crosslink density of network. Regarding
12 CAPE based on poly(oxytetramethylene) i.e. PTHF co-crosslinked with di-epoxy [23],
13 the less concentrated CAPE i.e. $\text{O}/\text{Ca} = 13.8$ barely approaches $0.1 \text{ mS}/\text{cm}$ at 90°C . Due to
14 a lesser solvating repeat unit than POE (lower DN), PTHF networks were found to
15 provide with LiTFSI, conductivities one order of magnitude lower [38]. In ref. [23], the
16 oligoTHF curing provides however, in average, through the di-epoxy ring opening 4 OH
17 group per kg increasing the AN of the network, thus its solvating ability. Comparing our
18 data with the few ones available reinforce our selection of a host polymer based on
19 oxyethylene repeat unit.

20 Data presented in Figure 6 were fitted by using the Vogel-Tamman-Fuelcher (VTF)
21 equation as elsewhere described [39]:

22

$$23 \quad \sigma(T) = A_0 T^{-1/2} \left(\frac{-E_a}{R(T-T_0)} \right) \quad (\text{eq. 2})$$

24

1 where $A_{0,i}$ is proportional to the number of charge carriers, $E_{a,i}$ is the pseudo-activation
2 energy for conduction and $T_{0,i}$ is the ideal thermodynamic glass transition temperature.
3 The pseudo-activation energy of conductivity is similar for all the Ca/O ratios (ca. 14.3
4 kJ/mol) with the exception of Ca/O = 16 (19.2 kJ/mol). These values are in accordance
5 with other studies for systems based on POE and LiClO₄ [40].
6 We extended this study to both POE-CaI₂ and POE-Ca(TFSI)₂ electrolytes, where O/Ca
7 = 30 and 40, corresponding to a Li polymer electrolyte of 15 and 20 respectively. In
8 addition to its intrinsic stability in reduction, CaI₂ has two main advantages, namely its
9 molar weight 294 g as compared to 338 g for Ca(CF₃SO₃)₂ and 600 g for Ca(TFSI)₂ and
10 its low cost. Regarding Ca(TFSI)₂, it was chosen to achieve a good comparison with
11 LiTFSI considered, since early work [41], as the reference salt in Li-POE electrolytes.
12 Figure 7 compares the Arrhenius plots of POE electrolytes based on CaI₂ and Ca(TFSI)₂.
13 Unfortunately, POE-CaI₂ exhibits poor conductivities, slightly exceeding 0.01 mS at 85°C
14 for the ratio O/Ca = 40. On the other hand, POE-Ca(TFSI)₂ polymer electrolytes revealed
15 ionic conductivities higher than those obtained with POE-Ca(CF₃SO₃)₂. Indeed, at 90°C,
16 the maxima ranged from 0.82 mS·cm⁻¹ (O/Ca = 30) to 0.48 mS·cm⁻¹ (O/Ca = 40).
17 However, these values are questionable as creeping occurs from 80 to 85°C for O/Ca 30
18 and 40, respectively. From these preliminary data, it can be inferred that Ca(CF₃SO₃)₂ is
19 the most suitable among the investigated Ca salts, in terms of conductivity, molar weight
20 and electrochemical window. Moreover, based on data obtained in Li-polymer
21 electrolytes, where the cationic transference number (T^+) of LiCF₃SO₃ is roughly 3 times
22 higher than that of LiTFSI [42], higher T^+ and, consequently, higher cationic
23 conductivity, σ^+ , can be expected for POE-Ca(CF₃SO₃)₂ electrolytes.

24

25 **3.6. Discussion**

1 Decreasing the flammability of high-capacity batteries is an important and current
2 challenge for their application in the automotive field and grid implementations. Whereas
3 in Li and Na batteries solid inorganic electrolytes can be a solution to improve safety, as
4 of today no ceramic or glassy electrolyte allows multivalent cations to move at least, in
5 the explored temperature range. This preliminary study validates the possibility to
6 dissolve, up to fairly high salt concentrations, three calcium salts in the reference host
7 polymer, POE. The choice of POE is dictated by the state of the art in lithium polymer
8 electrolytes. Indeed, it is assumed that if POE has demonstrated sufficient electrochemical
9 stability vs Li metal, it could be advantageously used with Ca metal. Additionally, POE
10 homo- and copolymers have an anodic stability close to 3.9 V vs Li/Li⁺ thus 3.72 V vs
11 Ca/Ca²⁺. Hence, they could be electrochemically stable with several cathodes previously
12 proposed. Thus, Ca²⁺ was reversibly inserted in nanocrystallized V₂O₅ [43] while
13 enhanced insertion in V₂O₅ nanocomposites compared to Li [44] was reported, validating
14 the capability of CaB to benefit from high-performing positive electrode materials. Even
15 though these validations were performed using liquid electrolytes, Gauthier *et al.* [45]
16 built and successfully tested Li/VO_x prototypes based on solvent-free polymer salt
17 complexes used both as polymer electrolytes and as binders of LiVO_x composite
18 cathodes, paving the way for the use of CAPE as binders for V₂O₅ cathode materials.
19 Whether the present work illustrates the feasibility in terms of salt solubility and
20 conductivity of POE electrolytes, it however also emphasizes their limitations in terms of
21 (i) crystallinity and T_m and (ii) mechanical properties (creeping from 80 to 85°C). These
22 limitations could be overcome by using amorphous polyether networks, which
23 demonstrated high conductivities as Li polymer electrolytes, while avoiding creeping
24 [33]. Nonetheless, information about cationic transference numbers, T⁺ is missing in this
25 paper as their determination currently faces two issues: (i) Ca²⁺ does not deposit onto Ca⁰;

1 this hinders the electrochemical determination from symmetric $\text{Ca}^0/\text{Ca-electrolyte}/ \text{Ca}^0$
2 cells [46][47]; and (ii) the inadequacy of Pulse Field Gradient NMR as a characterization
3 technique, as the main Ca isotope is not detected by NMR. Nonetheless, a cationic
4 transference number has recently been measured [23] using the impedance technique
5 [47]. This measurement at least exists even though we are fully convinced neither by the
6 shape of the polarization curve [23] (see supplementary information) nor by the
7 establishment of a steady-state current. Moreover the fairly high T^+ reported, 0.352, was
8 obtained for the concentration $\text{O}/\text{Ca} = 1.9$ (similar to O/Li #1) far from the usual salt
9 concentrations in polymer electrolyte-based batteries, falling more within the salt in
10 polymer concept. Regarding the mobility of alkaline-earth cations, Vincent reported that
11 Mg^{2+} moves together with oligoether chains having molecular weights below the
12 entanglement threshold ($\sim 3,200 \text{ g}\cdot\text{mole}^{-1}$) [48]. He also compared, by *d.c.* polarization
13 [49], the mobility of Mg^{2+} and Ca^{2+} hosted in oligomers ($M_n \gg 3,200 \text{ g}$) and linear
14 polymers (commercial POE and polycondensates), using mercury amalgams (Mg/Hg and
15 Ca/Hg) electrodes. Surprisingly, Vincent did not use the impedance technique that he
16 previously co-authored [47] to access T^+ . In both host polymers, Mg^{2+} was found to be
17 immobile. Conversely, an important current passed for more than 20 hours in the calcium
18 symmetric cell. Indeed, if alkaline cations, from Li^+ to K^+ , and alkaline-earth cations,
19 from Mg^{2+} to Ba^{2+} are both considered as Hard Acids (HSAB theory), one can infer that
20 Li^+ should have roughly the same hardness as Mg^{2+} when Ca^{2+} hardness should be close
21 to K^+ one. Since the ether function of ethylene oxide repeat unit is a Hard Base, a high
22 Acid Hardness should be more detrimental to the mobility of alkaline-earth cations
23 compared to alkaline cations, especially as the former have a double positive charge.
24 Besides Vincent, on the basis of water molecules exchanges, assumed a higher hardness
25 of Mg^{2+} vs Ca^{2+} , assumption in accordance with the reinforcement of thermoplastics,

1 elastomers and gels induced by MgO fillers [34]. A significant reinforcement above T_m ,
2 with regard to POE host, should be therefore induced by the dissolution of Ca and, above
3 all, of Mg salts. Nonetheless, even though both Ca^{2+} and Mg^{2+} triflate delay the creeping
4 of their related polymer electrolytes with regard to the POE host, this reinforcement, even
5 in the case of Mg triflate, is not noticeable with regard to POE/Na triflate [26] (*vide*
6 *supra*). As a tentative explanation, one can infer that both divalent cations are mainly
7 located inside POE (intra-chain solvation) minimizing inter-chain solvation and,
8 therefore, transient crosslinks. Based on macroscopic, *therefore questionable*, DMTA
9 data, this assumption is however supported by the crystallographic structure of
10 POE/ $HgCl_2$ complexes [35][36].

11

12 **4. Conclusions**

13 The experimental data presented in this work validate the use of liquid-free CAPE based
14 on the reference and commercially available poly(oxyethylene) (POE). All the calcium
15 salts tested in this work were found to be homogeneously dissolved in the POE host
16 polymer and we did not detect any microphase separation. The thermal stability of Ca
17 polymer electrolytes points to a very high level of safety; the conductivity levels beyond
18 the melting temperature, though not outstanding, are satisfactory for the intended
19 application. However, the proposed CAPE suffer from two main drawbacks: (i) low
20 conductivities from ambient temperature to T_m ; and (ii) an insufficient mechanical
21 strength, that prevents their processing into thin films. After validating the suitability of
22 POE chains as a macromolecular solvent, from now on we are aiming at improving room
23 temperature conductivities by using amorphous polyether networks prepared either from
24 polycondensates [33] or from POE copolymers [50][51]. Although these networks, due
25 to their three-dimensional nature, would allow the polymer electrolyte creeping to be

1 avoided, their processing into films 10 to 20 μm thick is challenging as it requires a high
2 density of crosslinks, that is detrimental to ionic conductivity [23][24]. Nevertheless,
3 nanocomposite strategies [52] based on the use of moderate wt% amounts of Crystalline
4 Nano Cellulose (CNC) should reconcile a high mechanical strength and high
5 conductivities, allowing the ohmic drop in the electrolyte to be decreased. Contrarily to
6 Li and even Na polymer electrolytes, the development of CAPEs still remains a
7 pioneering topic that requires intensive research efforts, *e.g.* exploration of new salts
8 benefiting from extended delocalization of the anionic charge [53], accurate
9 determination of cationic transference numbers, studies to elucidate the evolution of the
10 interface between Ca^0 and CAPEs based on various Ca salts, etc. This physicochemical
11 work paves the way for the development of improved polymer electrolytes able to conduct
12 Ca species.

13

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TABLES

Table 1. Relevant properties of Li, Na, K, Mg and Ca for battery applications [10].

Properties	Abundance in Earth's crust (g/kg)	Melting point, T_m (°C)	Density	Molar mass (g/mol)	Mass-to-electron ratio (g/mol of e^-)	Specific capacity (Ah/g)	Volumetric capacity (Ah/cm ³)	Redox potential (E_o in V vs SHE)
Li	0.02	180.5	0.53	6.9	7	3.86	2.06	-3.05
Na	23.6	98.0	0.97	23.0	23	1.16	1.12	-2.71
K	20.9	63.5	0.89	39.1	39	0.68	0.61	-2.92
Mg	23.3	650	1.74	24	12	2.20	3.80	-2.37
Ca	41.5	842	1.54	40	20	1.34	2.06	-2.87

Table 2. Melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (X_c) for POE-based polymer electrolytes at different O/Ca ratios.

O/Ca	POE-Ca(CF ₃ SO ₃) ₂			POE-CaI ₂			POE-Ca[TFSI] ₂		
	T_m °C	X_c %	ΔH_m J·g ⁻¹	T_m °C	X_c %	ΔH_m J·g ⁻¹	T_m °C	X_c %	ΔH_m J·g ⁻¹
16	52.5	12	26.5	-	-	-	-	-	-
20	54.4	14	30.6	-	-	-	-	-	-
30	59.1	30	64.7	71.5	29	63.9	64.6	18	39.2
40	63.3	34	72.1	69.5	44	95.3	70.8	24	51.1

1 **Table 3.** TGA measurements carried out under nitrogen for POE-CaX₂ polymer
 2 electrolytes.

POE-CaX ₂	T _{onset} (°C)	residue % 450°C	wt% of salt
POE-Ca(CF₃SO₃)₂			
O/Ca=8	397.8	51.4	49
O/Ca=16	395.2	36.1	32.4
O/Ca=20	387.5	31.9	27.8
O/Ca=30	386.4	25.1	20.4
O/Ca=40	383.1	21.4	16.1
POE-CaI₂			
O/Ca=30	347.3	21.9	18.2
O/Ca=40	344.6	20.7	14.3
POE-Ca(TFSI)₂			
O/Ca=30	357.0	8.3	31.3
O/Ca=40	385.9	8.8	25.4

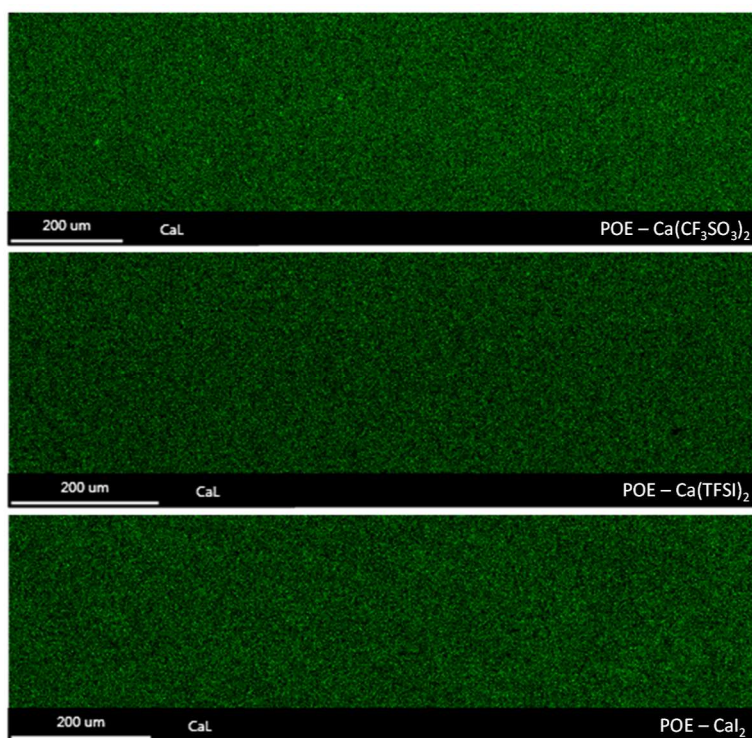
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FIGURES

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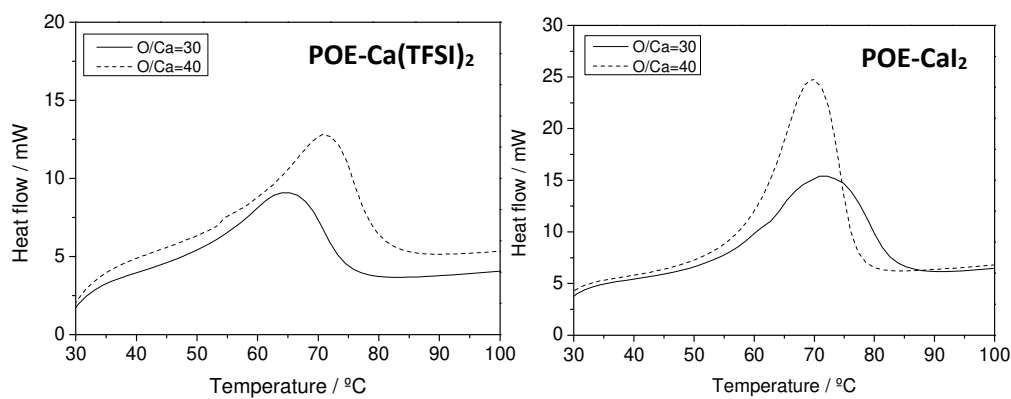
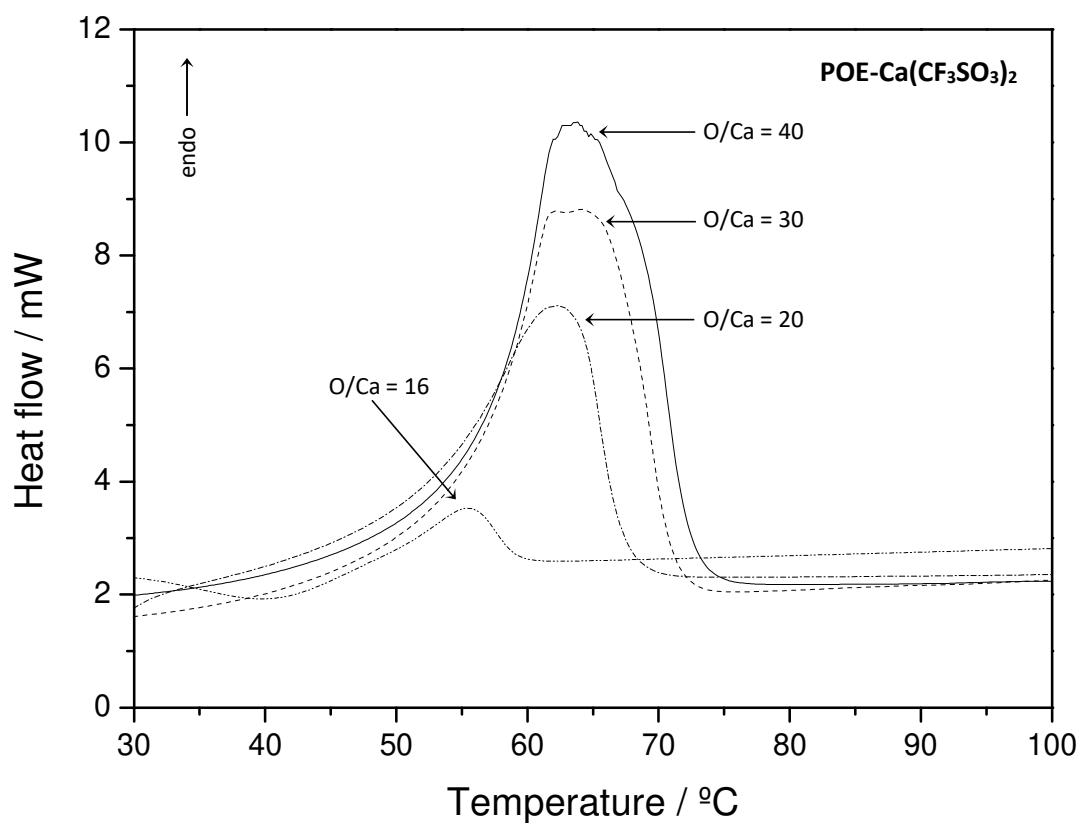
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4 **Figure 1.** Distribution of calcium obtained by X-ray mapping in the proposed
5 electrolytes. Top panel: POE-Ca(CF₃SO₃)₂; middle panel; POE-Ca(TFSI)₂; bottom panel:
6 POE-CaI₂. All the samples exhibit an O/Ca molar ratio equal to 30.

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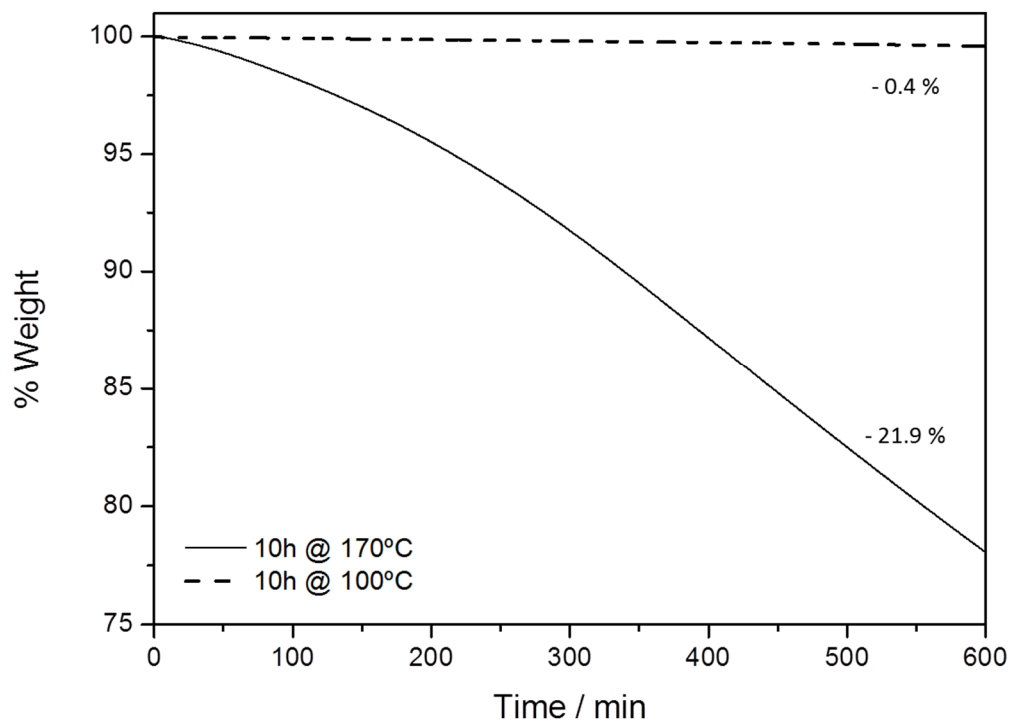


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2 **Figure 2.** DSC measurements showing the effect of salt concentration and type on
 3 melting temperature (T_m) of the different POE-based calcium polymer electrolytes.

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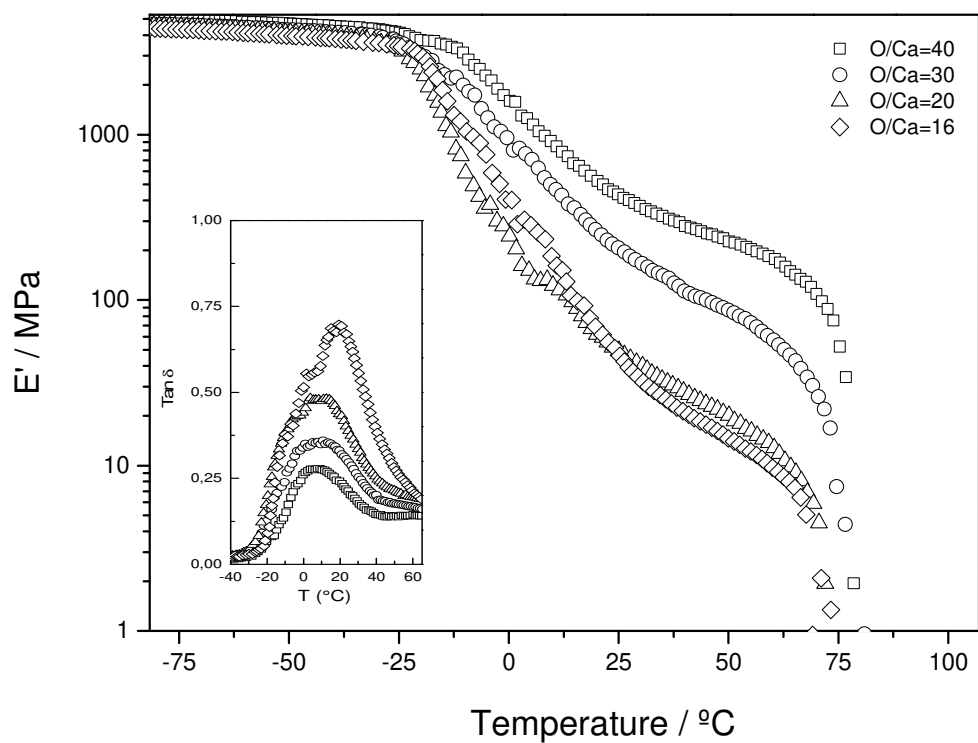
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3 **Figure 3.** Isothermal TGA analyses of POE-Ca(CF₃SO₃)₂ carried out at 100 and 170°C

4 in a mixture of air and nitrogen.

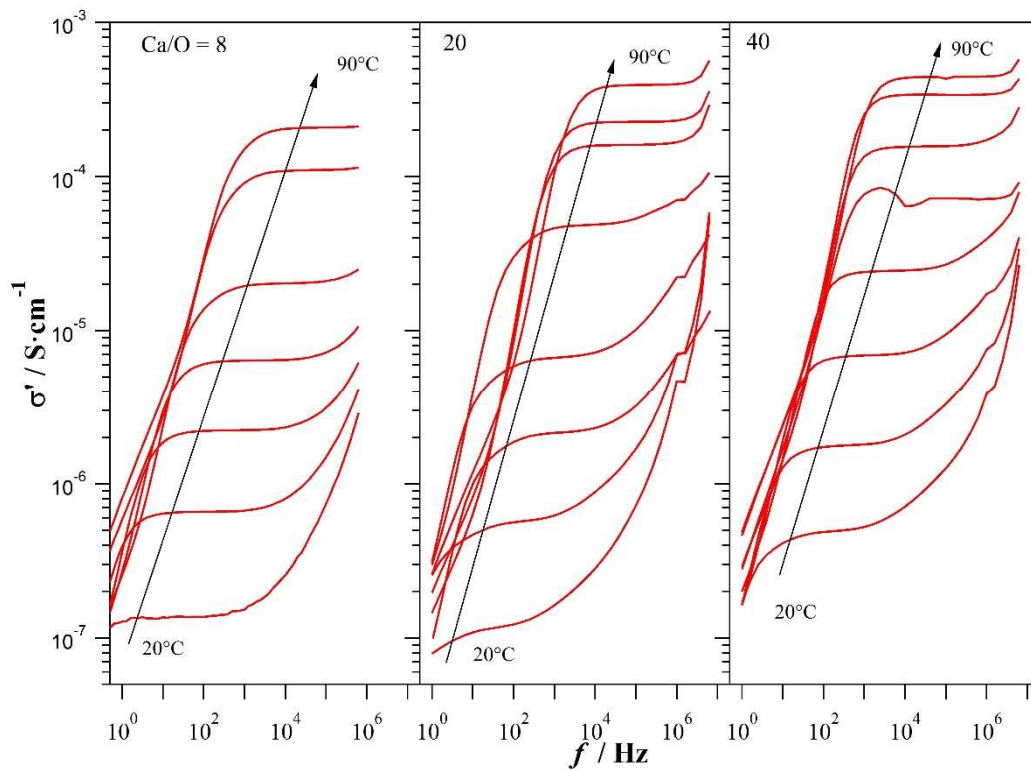
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Figure 4. Storage moduli (E') obtained by DMTA for POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ electrolytes at different O/Ca ratios. The inset shows peaks corresponding to the $\tan \delta$ of the electrolytes as temperature is raised.

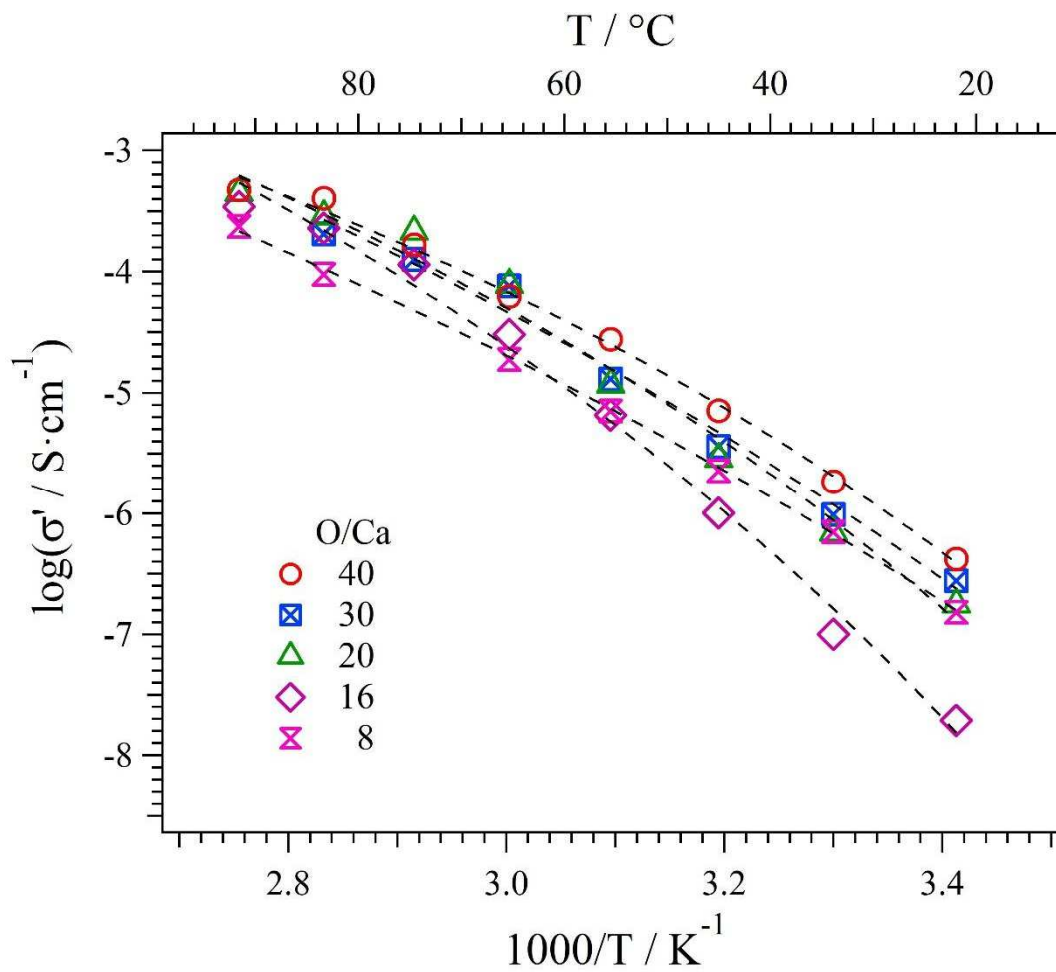


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2 **Figure 5.** Real component of the complex conductivity (σ') vs frequency and temperature

3 for POE- $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ samples ($\text{O}/\text{Ca} = 8, 20, 40$).

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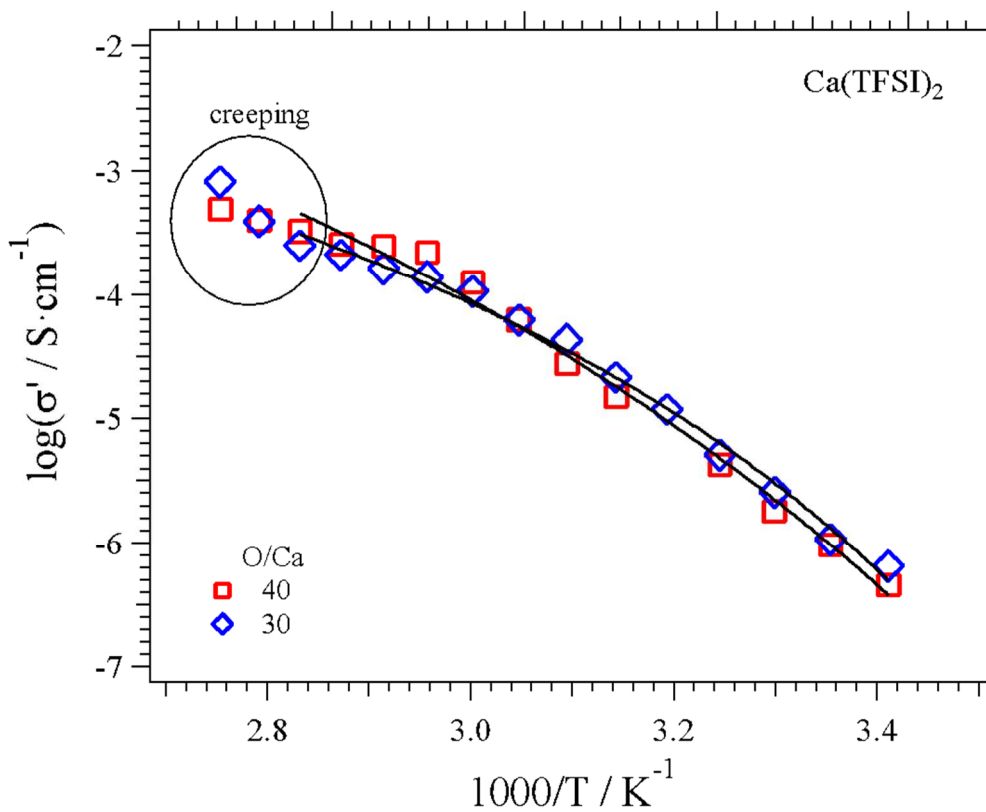
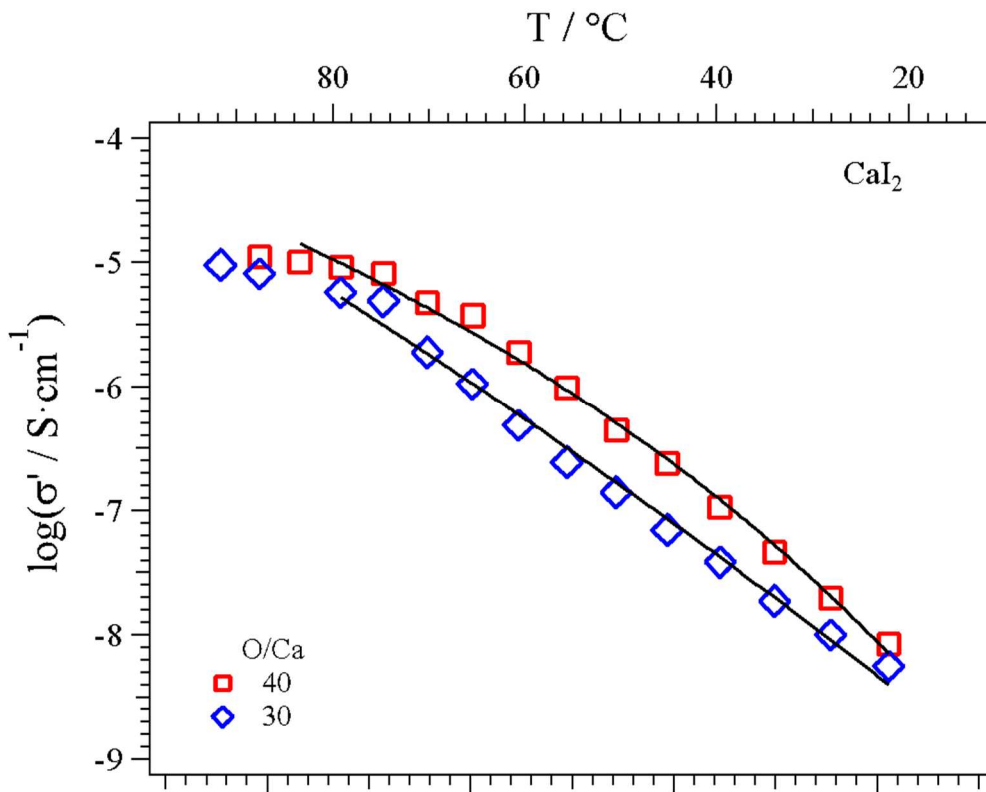


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2 **Figure 6.** Ionic conductivity as a function of temperature and O/Ca ratio for POE-
 3 $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ samples.

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3 **Figure 7.** Ionic conductivity as a function of temperature and O/Ca ratio for POE- CaI_2

4 and POE- $\text{Ca}(\text{TFSI})_2$ electrolytes. Dotted lines correspond to VTF fitting.