Solubilization of SEI lithium salts in alkylcarbonate solvents

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ABSTRACT

The SEI (Solid Electrolyte Interphase) at the surface of electrodes in lithium-ion batteries is composed of various lithium compounds, organic or mineral, which have a direct impact on cycling performance. The main lithium species constituting the SEI and selected in this study are lithium fluoride LiF, lithium carbonate Li_2CO_3, lithium hydroxide LiOH, lithium oxide Li_2O, lithium methoxide $LiOCH_3$ and lithium ethoxide $LiOC_2H_5$. Their solubilities were determined in ethylene, propylene, dimethyl, diethyl and vinylene carbonates (EC, PC, DMC, DEC and VC) and in one of their mixtures commonly used in lithium-ion batteries (EC/PC/3DMC) by mean of atomic absorption spectroscopy (AAS). These solutions were also investigated by EIS (Electrochemical Impedance Spectroscopy) and conductimetry measurements. Results show that while solubilization properties differ between LiF and other lithium compounds considered, their association pattern in solution is identical and solutions are mainly constituted of quadrupolar aggregates.

1. Introduction

Understanding the role of each component of the SEI (Solid Electrolyte Interphase) at the surface of electrodes is essential to determine the effect of these passivation films on cycling performance of lithium-ion batteries. Though the composition and structure of the SEI has been comprehensively studied [1–4], the influence of its constituents on battery efficiency is still unclear. Even basic data, such as the solubility of these compounds in the electrolyte, is practically inexistent in literature to this day as most of the solubility studies have been carried out in protic solvents [5–9]. The purpose of this work is to determine which SEI species are most soluble (therefore potentially less damaging to battery cycling), and how these species are organized in alkylcarbonate solvents used in the electrolyte.

Previous study showed that lithium fluoride, one of the main constituents of the SEI, presents a unique dissolution behavior in alkylcarbonate solvents, driven by entropic interactions between the salt and solubilizing media [10]. EIS (Electrochemical Impedance Spectroscopy) investigations on LiF solutions in ethylene and propylene carbonate demonstrated that lithium fluoride is organized as quadrupolar aggregates in these solvents [11]. The question remains as to whether other lithium salts constituting the SEI present similar properties towards solubility and association in alkylcarbonates. The compounds selected for this work are lithium carbonate Li_2CO_3, lithium hydroxide LiOH, lithium oxide Li_2O, lithium methoxide $LiOCH_3$ and lithium ethoxide $LiOC_2H_5$. These species are omnipresent in the SEI when cycling on graphite and $LiCoO_2$ electrodes with the commonly used electrolyte: $LiPF_6$ at $1\,mol\,L^{-1}$ in EC/PC/3DMC w/w (ethylene, propylene and dimethyl carbonates). These compounds are also commercially available.
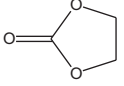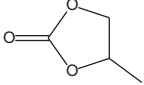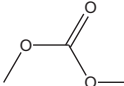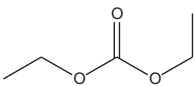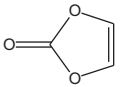
LiF is inevitably present when using fluorinated lithium salts such as $LiPF_6$ in the electrolyte. Indeed, even at ambient temperature there is equilibrium between $LiPF_6$ and $LiF + PF_5$ [12]. The formation of lithium fluoride is favored by elevated temperature and water contamination of the electrolyte [13–15]. As to lithium alkoxides $LiOCH_3$ and $LiOC_2H_5$, they are reduction products of acyclic carbonates such as DMC [12,16,17], while lithium carbonate is formed by the reduction of cyclic carbonates (EC and PC) [18–20] and of DMC [2,3]. The formation of lithium hydroxide results from the presence of H_2O traces in the electrolyte [12]. Lithium oxide is formed by the reduction of LiOH, and is therefore frequently found in the SEI [12]. All of these compounds are present in the passivation layer on graphite electrode, but LiF and Li_2CO_3 are also found at the cathode surface [13,21].

The study of LiF solubility in alkylcarbonates, described in a previous paper for EC, PC and DMC [10], is completed in this work with other carbonate solvents: VC (vinylene carbonate) which is often employed as an additive, DEC (diethyl carbonate) and the ternary mixture EC/PC/3DMC, commonly used in lithium-ion batteries.

Table 1
Properties of alkylcarbonates studied in this work at 25 °C.

Solvent	Structure	Molar mass (g mol^{-1})	Melting point T_m (°C)	Boiling point T_b (°C)	Viscosity η (cP)	Dielectric constant ε	Dipole moment μ (D)	Density ρ (g cm^{-3})
EC		88	36.4	248	1.90 (40 °C)	89.78	4.61	1.321
PC		102	−48.8	242	2.53	64.92	4.81	1.200
DMC		90	4.6	91	0.59 (20 °C)	3.11	0.76	1.063
DEC		118	−74.3	126	0.75	2.80	0.96	0.969
VC		86	22	162	–	127	4.55	1.355

Focus was made on lithium fluoride because of its preponderance within the SEI and its high solubility in alkylcarbonates compared to other lithium compounds. Concerning other SEI compounds (Li$_2$CO$_3$, LiOH, Li$_2$O, LiOCH$_3$ and LiOC$_2$H$_5$), their solubility and conducting properties were studied in EC, PC, DMC and EC/PC/3DMC.

2. Experimental

2.1. Materials

The carbonate solvents EC, PC, DMC, DEC and VC were purchased from Aldrich, with purity >99%. Lithium salts (lithium fluoride LiF, lithium carbonate Li$_2$CO$_3$, lithium hydroxide LiOH, lithium oxide Li$_2$O, lithium methoxide LiOCH$_3$ and lithium ethoxide LiOC$_2$H$_5$) were also purchased from Aldrich and used as received (purity >95%). All reagents are stored in a glove box under Argon atmosphere. The water content of all solutions was less than 20 ppm, as indicated by Karl Fischer measurements.

2.2. Apparatus and procedure

A Thermo MSeries FS95 atomic absorption spectrophotometer was used for solubility determinations. A lithium hollow-cathode source, with a selected wavelength of 670.8 nm, was employed for measurements. The analytical procedure has been fully described in a previous paper [10].

Scanning Electron Microcopy (SEM) was performed on lithium compounds with a Zeiss DSM 982 Gemini device. Samples were deposited on a carbon coating and metalized with 5–8 nm of platinum under vacuum ($P = 5$ Pa).

Laser diffraction granulometry characterizations were carried out with a Mastersizer 2000 from Malvern Instruments, with particle detection ranging from 0.02 to 2000 μm. Results are the average of 5 measures, and reflect size distribution of micrometric particles, since nanometric species are not visible with this method and are concealed in background noise.

Conductivity measurements were performed using a Crison GLP 31 conductimeter operating at variable frequencies, equipped with platinum electrodes covered by platinum black (cell constant: 0.1 cm^{-1}). Solutions were thermostated in double-wall cells during analysis. Temperature variation of the samples was $\Delta T \pm 0.1$ °C. Samples were prepared by adding increasing masses of lithium salt to the solvents.

EIS measurements were performed with a Solartron 1260 impedancemeter, over the frequency range 1–10^7 Hz with a 10 mV sinusoidal voltage. The solutions are characterized between two stainless steel blocking electrodes in thermostated cells, with a temperature variation of $\Delta T \pm 0.3$ °C and a cell constant of 0.0545 cm^{-1}.

Measurements in PC, DMC and EC/PC/3DMC were made at 20 °C. In EC, measurements are taken at 40 °C because of the high melting point of this solvent ($T_m = 36$ °C).

3. Results and discussion

3.1. Solubility determination

3.1.1. Lithium fluoride

Solubilities of LiF in EC, PC and DMC were determined previously [10]. Solubility values were measured at 20 °C in DEC, VC and the ternary mixture EC/PC/3DMC. The main properties of these solvents are presented in Table 1 [22]. It must be noted that VC is mostly used as an additive rather than a solvent in lithium-ion batteries. Solubility results for LiF obtained from atomic absorption measurements at 20 °C are given in Table 2, along with previous data obtained in EC, PC and DMC [10]. Solubility values vary greatly according to the solvent, despite the fact that all these solvents belong to the alkylcarbonate family. While lithium fluoride is practically insoluble in DEC, is it very soluble in the ternary mixture ($s > 9$ g L^{-1}). The solubility value obtained in VC is close to that obtained in PC (0.13 g L^{-1} at 20 °C), probably because of the similarity of their structure: VC exhibits a double bond which induces steric encumbrance similar to that of the methyl group in PC. It was also shown

Table 2
Solubility of lithium fluoride in alkylcarbonates at 20 °C.

Solubilizing medium	Solubility ± 0.01 (g L^{-1})	Solubility ± 4 × 10^{-4} (mol L^{-1})
EC (40 °C) [10]	5.52	2.123 × 10^{-1}
PC [10]	0.13	5.0 × 10^{-3}
DMC [10]	0.57	2.19 × 10^{-2}
DEC[a]	<0.01	<4 × 10^{-4}
VC[a]	0.20	7.7 × 10^{-3}
EC/PC/3DMC[a]	9.08	3.492 × 10^{-1}

[a] This work.

Table 3
Solubility of lithium salts in alkylcarbonates at 20 °C.
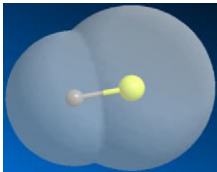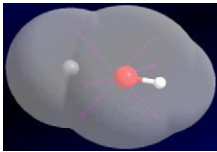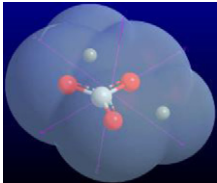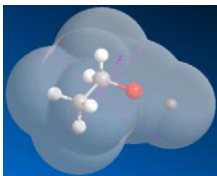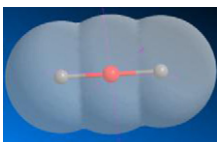
Lithium compound	Solubility ± 0.01 (g L^{-1})			
	PC	EC (40 °C)	DMC	EC/PC/3DMC
Li_2CO_3	0.19	0.87	0.09	0.04
LiOH	0.59	1.37	0.05	0.06
Li_2O	0.04	–	0.01	0.01
$LiOCH_3$	0.05	0.64	0.09	0.01
$LiOC_2H_5$	0.02	0.12	0.30	0.09

in a former paper [10] that the solubilization mechanism for LiF in alkylcarbonates is entropy-driven and strongly dependent on the structure of these solvents upon salt addition. This phenomenon could explain the large disparity in solubility values obtained for lithium fluoride in alkylcarbonates. The enhanced solubility of LiF in EC/PC/3DMC could be explained by favorable Van der Waals interactions between the solute and the ternary mixture.

3.1.2. Other lithium compounds

The solubility of other lithium compounds (Li_2CO_3, LiOH, Li_2O, $LiOCH_3$ and $LiOC_2H_5$) was measured by atomic absorption in PC, DMC and the ternary mixture EC/PC/3DMC at 20 °C, and in EC at 40 °C because of its high melting point. Results are given in Table 3. AAS measurements for Li_2O were performed without dilution in water of the samples, to avoid the formation of LiOH. Its solubil-

Table 4
Structural properties of lithium compounds.

Compound	μ (D)	Mulliken charge	Molecular volume (cm^3 mol^{-1})	Solvation sphere
LiF	6.55	Li 0.74 F −0.74	22.2	
LiOH	4.21	O −0.69 H 0.00 Li 0.69	22.2	
Li_2CO_3	7.43	Li 0.75 C 1.06 O$_{(1 and 2)}$ −0.79 O$_{(3)}$ −0.97	47.9	
$LiOCH_3$	<u>4.87</u>	C 0.26 O −0.97 H 0.00 Li 0.71	20.6	
$LiOC_2H_5$	5.09	C$_{(1)}$ −0.06 C$_{(2)}$ 0.33 O −0.97 H 0.00 Li 0.70	57.2	
Li_2O	0.00	Li 0.56 O −1.13	33.9	

ity in EC could not be determined because it solidifies at ambient temperature unless it is diluted with water. Lithium compounds considered are generally much less soluble than LiF, especially in the ternary mixture ($s < 0.09\,g\,L^{-1}$). Lithium oxide is one of the less soluble salts in alkylcarbonates, with solubility values below $0.05\,g\,L^{-1}$ in all media. As it was noticed before for LiF, EC exhibits an important solubilizing power towards lithium salts, which results at least partially from its high dielectric constant (89.8 at 25 °C) [22].

The low solubility of lithium salts considered, at the exception of LiF, could result from a combination of anion size and dipole moment effects. The geometries of these lithium salts were optimized using the Monte-Carlo method with restricted Hartree-Fock RHF/6-31G (Chemdraw® software with Gaussian program). Properties such as Mulliken atomic charge, dipole moment (using field-independent basis), and molecular volume (based on $0.001\,e/bohr^3$ density envelope) were determined for these compounds. The results obtained are presented in Table 4. Dipole moments of lithium salts considered are all above 4 D, at the exception of Li_2O which exhibits a null dipole moment. This means that these compounds are strongly polar. The molar volume in vacuum is about $20\,cm^3\,mol^{-1}$ for $LiOCH_3$, LiF and LiOH, and is com-

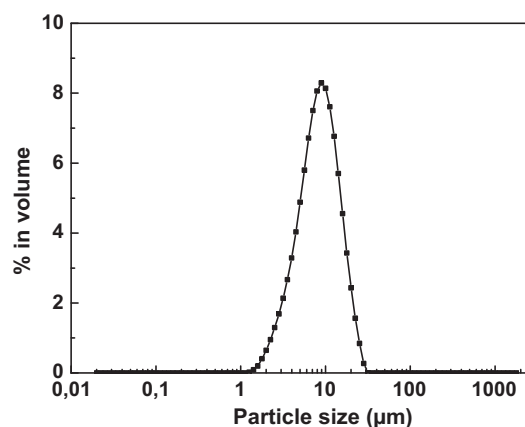**Fig. 1.** Particle distribution for a LiF solution in PC at saturation.

prised between 34 and 57 $cm^3\,mol^{-1}$ for Li_2O, Li_2CO_3 and $LiOC_2H_5$. The atomic charge presents large variations from one species to another, as the charge born by Li varies from 0.56 to 0.75, and by oxygen from -1.13 to -0.69. The solvation sphere of each molecule,
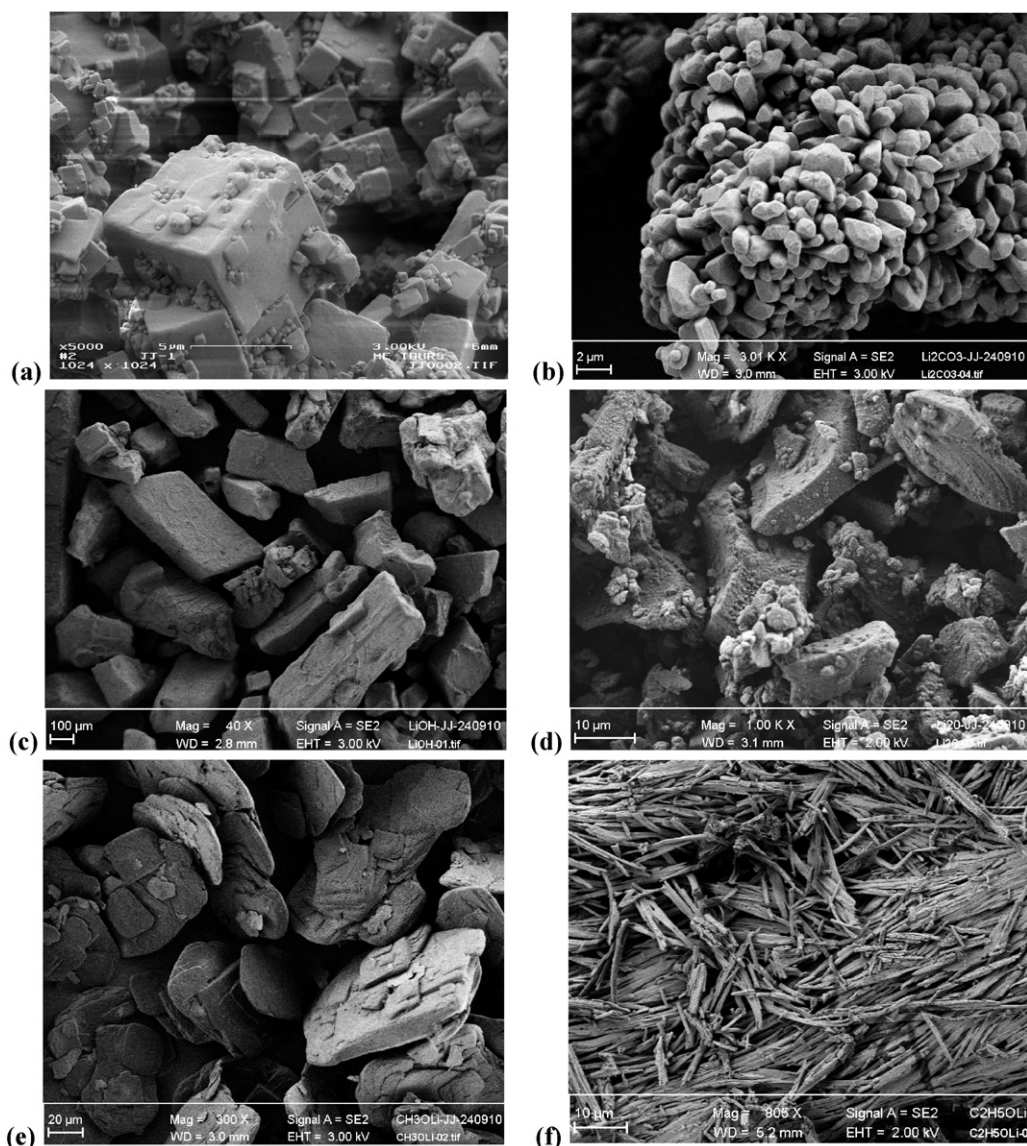

Fig. 2. SEM pictures of lithium compounds studied: LiF (a), Li_2CO_3 (b), LiOH (c), Li_2O (d), $LiOCH_3$ (e) and $LiOC_2H_5$ (f).
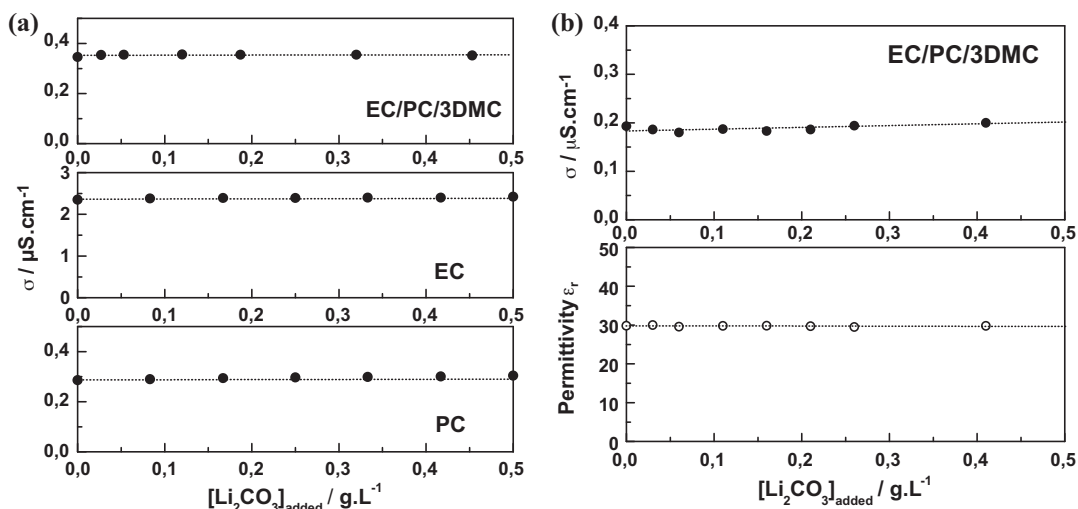
Fig. 3. Evolution of conductivity (σ) and electrical permittivity (ε) at 20 °C of Li_2CO_3 solutions in alkylcarbonates with salt addition. Results are obtained by conductimetry (a) and by EIS (b).

schematized in Table 4, is related to the volume occupied by the compound in solution. This data does not allow determining which parameters control solubilization properties of lithium compounds in alkylcarbonates. Indeed, LiF and $LiOCH_3$ for example exhibit similar dipole moment, lithium charge and molar volume, but their solubility behavior is radically different.

3.1.3. Effect of particle size on solubility data

When studying dissolution phenomena, it is important to take account not only the nature of the solubilizing medium, but also the impact of the solute's size on solubility data. Indeed, different kinds of solubility may be measured according to analytical method. Colloidal solubility takes into account the contribution of nanometric particles, while non-colloidal solubility (or true solubility) is related to species above colloidal size [23,24]. Filtration of solutions can lead to colloid adsorption and aggregation, hence lower solubility values are obtained as evidenced by Tasaki [25]. In this study, the contribution of colloids is taken account, solubility data given in this paper corresponds therefore to the colloidal solubility of considered solutions.

The relation between particle dimension and solubility is described by the Ostwald–Freundlich equation [26,27], which is the transposition of the Gibbs–Kelvin equation for a solid–liquid mixture [28], and is written as follows:

$$\ln\left[\frac{s}{s_0}\right] = \frac{4}{\nu}\frac{\gamma_{SL}}{D_p}\frac{V_m}{RT}$$

s is the solubility of small spherical particles, s_0 is equilibrium solubility (particles of infinite radius), γ_{SL} is the solid–liquid surface tension, V_m is the molar volume of particles, $\nu = \nu^+ + \nu^-$ is the number of ion moles for a mole of solute, D_p is the particle diameter, R the gas constant and T the temperature.

This equation has been established for spherical particles of constant curvature and therefore cannot be directly applied to lithium fluoride, for which most of the particles are not sphere-shaped but cubic. Nevertheless, as predicted by Kelvin's law, the solubility of LiF in alkylcarbonates is a function of the size of the particles. Indeed, before determining solubility by AAS, saturated solutions of LiF in PC have been filtrated to check the effect of particle size on solubility. Filtration was performed on ceramic filtering crucibles, with porosity ranging from 4 to 40 μm. Solubility results are presented in Table 5 as a function of the filter pore size. When filtering with pore size above 17 μm, solubility values are identical to those obtained

Table 5
Solubility values for LiF in PC at 25 °C, according to filtration.

Filtration mode	Pore size (μm)	Solubility (g L^{-1})
Without	–	0.14
Size 3 crucible	17–40	0.14
Size 4 crucible	11–16	<0.01
Size 5 crucible	4–10	<0.01

without filtration, but with pore size below 16 μm the solubility becomes close to zero. LiF particles are hence mostly superior to 16 μm in diameter. This experiment was completed by granulometry measurements on a saturated solution of lithium fluoride in PC, which indicate that solute particles have an average 10 μm diameter (Fig. 1). The variation in LiF particle size between solubility and granulometry determinations may be attributed to colloid adsorption and aggregation upon filtration of the saturated solutions. Particle size has direct impact on measured solubility, in agreement with Kelvin's law. This phenomenon is confirmed by a conductimetric study from Tasaki on the solubility of lithium salts in DMC [25]. Solubility data presented in this work, obtained by passing saturated solutions on a 2 μm filter, are much lower than solubility values determined in the present paper (Table 6). These results show an indubitable link between solute size and solubility. The advantage of not filtering saturated solutions is that colloidal aggregates present in solution are not adsorbed or retained on the filter. Therefore, solubility data determined without filtration reflects in a more realistic way the behavior of solutions studied in this work. Indeed, lithium compounds studied in this work were characterized by SEM and show the presence of submicronic particles (Fig. 2). From these SEM pictures, it appears that lithium fluoride shows low particle size, with crystalline cubic elements as small as 500 nm, while other lithium compounds are mainly constituted of micro-

Table 6
Comparison of solubility values of lithium salts in DMC at 25 °C, with and without filtration.

Salt	Solubility with filtration $\pm 10^{-4}$ (mol L^{-1})	Solubility without filtration $\pm 10^{-4}$ (mol L^{-1})
LiF	2×10^{-4} [25]	2.19×10^{-2} [10]
Li_2CO_3	1×10^{-4} [25]	3.5×10^{-3} [this work][a]
LiOH	7×10^{-4} [25]	1.9×10^{-3} [this work][a]

[a] At 20 °C.
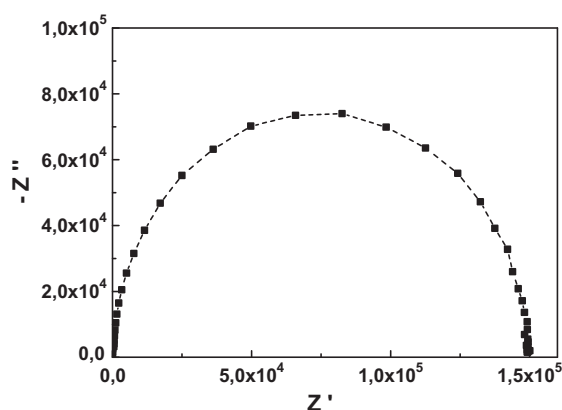
Fig. 4. Nyquist plot obtained for LiF in EC/PC/3DMC at $1.6\,g\,L^{-1}$ ($0.06\,mol\,L^{-1}$) at $20\,^{\circ}C$.

metric particles of various shapes. It is therefore important to take account the presence of these small LiF particles in alkylcarbonate solutions because they contribute to solubility values.

3.2. Electrochemical characterizations

Solutions of lithium compounds in alkylcarbonates were characterized by EIS and by conductimetry to determine their organization and dissociation pattern [11]. Results obtained were identical for all lithium salts (LiF, Li_2CO_3, LiOH, Li_2O, $LiOCH_3$ and $LiOC_2H_5$), for solutions prepared in EC, PC, DMC and EC/PC/3DMC. There is no dissociation of the lithium compounds in any medium, as indicated by the stability of conductivity values upon salt addition. Therefore, the presence of conducting species such as free ions or triple ions is unlikely in the considered media. No evolution of electrical permittivity with salt addition was observed neither, hence indicating the formation of apolar species in solution. Conductimetry and EIS results obtained for Li_2CO_3 solutions in alkylcarbonates are presented in Fig. 3. The resistive nature of lithium salt solutions in alkylcarbonates is evidenced by the semicircle shape of their Nyquist plots determined by EIS (Fig. 4). In agreement with results obtained for LiF in EC and PC [11], all lithium compounds considered seem to be organized in alkylcarbonate solvents as quadrupoles or higher aggregates, which are nonconductive and apolar. Lithium salts with high dipole moments ($\mu > 4\,D$, except for Li_2O) are associated at least as ion pairs of opposite charge. The dipole–dipole energy is sufficiently high to prevent any dissociation, even in high permittivity solvents such as EC and PC ($\varepsilon > 60$).

4. Conclusion

We have shown that SEI lithium compounds (Li_2CO_3, LiOH, Li_2O, $LiOCH_3$ and $LiOC_2H_5$) are weakly soluble in alkylcarbonates ($s < 1\,g\,L^{-1}$), as opposed to lithium fluoride. In particular, their solubilization behavior is completely different in the ternary mixture EC/PC/3DMC, where their solubility is very low in opposition to LiF ($s = 0.35\,mol\,L^{-1}$). One of the less soluble compounds is lithium oxide, which has a null dipole moment as opposed to other salts which are strongly polar ($\mu > 4\,D$). In agreement with previous observations for LiF, EC is the most solubilizing solvent for lithium compounds considered due to its high dipole moment ($\varepsilon = 89.8$).

The organization of the SEI compounds considered in alkylcarbonates is nevertheless identical to that of lithium fluoride, with a tendency to aggregate in apolar and non conductive species, with a quadrupole basic structure.

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