Deliverable 6.4

First Report on the characterization of electrolytes

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PU	**Public**	**x**
CO	**Confidential, only for members of the consortium (including the Commission Services)**	
CI	**Classified**	

Electrolytes

This report summarizes the characterization of Generation I of electrolyte (D2.2), which includes three separate electrolyte formulations:

- a highly fluorinated electrolyte based on 1M $LiPF_6$ in ethylene carbonate (EC) / ethyl methyl carbonate (EMC) (3:7, v/v) with fluoroethylene carbonate (FEC) and vinylene carbonate (VC) as additives
- a second fluorinated electrolyte in which 10% of the EC:EMC mixture has been replaced with oligomers of trimethylene carbonate
- a non-fluorinated electrolyte based on 0.7 M LiBOB in EC/EMC (3:7) and VC as additive

Ion diffusion, transference number and ionic conductivity

The ion transport properties of the electrolyte formulations were assessed using pfg-NMR spectroscopy. This was performed on ^7Li for Li^+ ions and ^{19}F for PF_6^- ions. For the BOB anions of the non-fluorinated electrolyte, the relaxation time of ^{11}B proved to be too short to enable diffusion measurements and ^{13}C, corresponding to the carbonyl carbons, was instead used for the BOB anions. The results are presented in Table 1.

Table 1. Diffusion data from pfg-NMR.

	$D(^7Li)$ / m^2 s^{-1}	$D(^{13}C)$ / m^2 s^{-1}	$D(^{19}F)$ / m^2 s^{-1}	T_+
LP57 + FEC + VC + oligomers	7.28×10^{-10}		5.90×10^{-10}	0.55
LP57 + FEC + VC	7.25×10^{-10}		5.53×10^{-10}	0.57
LiBOB + VC	1.39×10^{-9}	3.91×10^{-9}		0.26

The cation transference number T_+ was calculated according to

$$T_+ = \frac{D_+}{D_+ + D_-}$$

The values of the cation and anion diffusion coefficients were taken from the respective data for the different nuclei determined by pfg-NMR.

The ionic conductivity of the electrolytes was measured with a conductivity meter. The highly fluorinated electrolyte presented a higher conductivity than the non-fluorinated, 9.2 vs. 6.3 mS cm^{-1}, respectively.

These results indicate that despite the higher diffusion coefficients for the non-fluorinated electrolyte, their cation transference number and ionic conductivity were lower, suggesting that there is a stronger coordination of lithium ions to the BOB anion than to the PF_6^- ions, leading to the formation of ion pairs and clusters that do not contribute to the ionic conductivity (but that will move by diffusion). However, there is also the effect of the lower concentration of the non-fluorinated electrolyte (0.7 M) compared to the highly fluorinated electrolyte (1 M). It is also notable that replacing 10% of organic solvents with oligomers did not have a large impact on the ion transport properties of the electrolyte.

Advanced cell cycling characterization

Full cells have been investigated with the aforementioned electrolyte formulations and different electrode compositions. Firstly, the cells were composed of aqueous processed Si–graphite electrodes and organic processed NMC622, both provided by Varta. The silicon anodes correspond to the first generation materials containing 25% silicon with LiPAA as binder and carbon black as conductive agent without calendering. The cells were cycled galvanostatically

at C/20 for two initial cycles and then at C/2 while at the same time monitoring the evolution of the internal resistance using intermittent current interruption (ICI).

Figure 1 shows the electrochemical performance of the full cells with the three different electrolytes. During pre-cycling at C/20, the cells with the different electrolytes featured similar electrochemical performance. However, when increasing the C-rate to C/2 the cell with oligomers in the electrolyte suffered a rapid capacity fade mainly due to an increase in resistance, as seen from the large overpotential after 20 cycles.
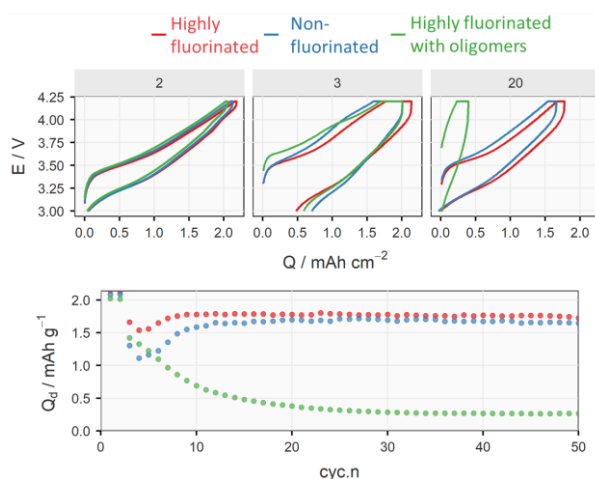
Figure 1. Voltage profiles at cycles 2, 3 and 20 (top) and discharge capacity (bottom) of full cells containing first generation Si–graphite anode and organic processed NMC622 cathode with a highly fluorinated electrolyte, a highly fluorinated electrolyte with oligomers and a non-fluorinate electrolyte.

Furthermore, the highly fluorinated and non-fluorinated electrolytes were tested in full cells containing an aqueous-processed NMC622 provided by CEA Liten and compared to the organic-based NMC622 electrode. For these tests, a reference silicon–graphite composite anode was used, with 25% silicon, LiPAA as binder and carbon black as conductive additive. Figure 2 shows the electrochemical performance of the full cells with the two cathodes and electrolytes. Cells containing organic-processed NMC622 cycled with both electrolytes showed similar capacity retention (73% after 400 cycles). In the case of the aqueous-processed NMC622, the fluorinated electrolyte featured slightly higher capacity retention than the fluorine-free electrolyte, 73% and 70%, respectively, after 400 cycles. Despite the similar performance of these electrolytes, the cell resistance of the cell with the fluorine-free electrolyte was slightly higher than for the fluorinated electrolyte.
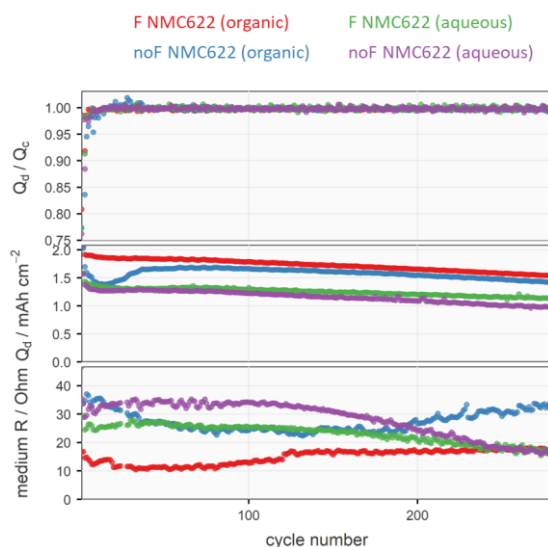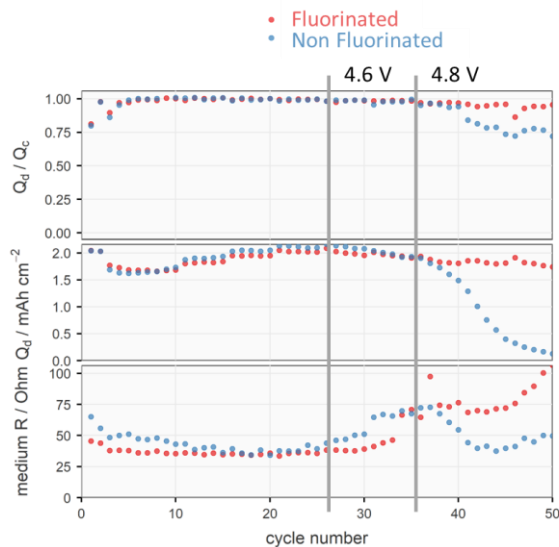
Figure 2. Electrochemical performance of full cells containing reference Si–graphite anode and NMC622 cathode processed in organic- and aqueous-based solutions with highly fluorinated (F) and fluorine-free (noF) electrolytes.

Formation of interphase layers

Post mortem analysis was carried out with X-ray photoelectron spectroscopy to determine the chemical composition of the passivating layers formed on the electrodes after 280 cycles. The main differences between the two electrolytes on the anode's surface is the presence of fluorinated species as well as nickel residues when using a highly fluorinated electrolyte. The latter confirms nickel dissolution from the cathode, which could be due to the presence of HF formed as part of the degradation reactions of the fluorinated electrolyte, followed by its deposition on the anode. In the case of the fluorine-free electrolyte, such nickel dissolution is not observed which could be due to the absence of HF as well as a better coating layer formed on the cathode by LiBOB that protects the migration of the nickel ions. In contrast, the SEI layer formed with the fluorine free electrolyte is mostly composed of boron, carbon and oxygen species. The main differences on the cathode is the thicker CEI layer formed with a fluorine-free electrolyte compared to the highly fluorinated electrolyte. The layer formed with the fluorine-free electrolyte is composed of boron and O=C–O species from the degradation of LiBOB, while the highly fluorinated electrolyte forms a CEI composed of fluorine and oxygen species. The thicker CEI layer appears to be the origin of the higher internal resistance observed with the fluorine-free electrolyte. The key to improving the performance of this electrolyte is thus not primarily to increase its ionic conductivity, but to optimize the formation of a thin but efficient CEI layer that can transport Li$^+$ ions efficiently.

Electrochemical stability

The oxidative stability of the fluorinated and the non-fluorinated electrolyte was characterized with the cut-off increase cell cycling (CICC) method. In these measurements, the cut-off voltage of the cell is increased every 5 cycles and the capacity and coulombic efficiency are monitored to check the appearance of side reactions. This effectively characterizes the electrochemical stability of the full system, including both the electrolyte and the electrodes. These experiments were carried out in full cells containing the first generation materials containing 25% silicon with LiPAA as binder and carbon black as conductive agent without calendering. The data from these experiments, shown in Figure 3, indicate that both cells with the two electrolytes suffered from side reactions at 4.6 V and a faster capacity fade was observed after 4.8 V. These results indicate that both electrolytes have similar anodic stability in the NMC622/Si–graphite full cells.

Figure 3. Electrochemical results with CICC method of full cells containing first generation Si–graphite anode and NMC622 cathode processed in organic-based solutions with fluorinated and fluorine-free electrolytes.

Conclusions

Similar electrochemical performance has been obtained with the fluorine-free as electrolyte compared to the highly fluorinated electrolyte, despite the differences in ion transport properties. However, the battery ageing and the decomposition products are different for each electrolyte. This suggests that fluorine-rich passivation layers are not required and stable (but so far more resistive) layers can also be formed with more environmentally friendly and less toxic electrolytes, such as fluorine-free alternatives.