Online Electrochemical Mass Spectrometry of High Energy Lithium Nickel Cobalt Manganese Oxide/Graphite Half- and Full-Cells with Ethylene Carbonate and Fluoroethylene Carbonate Based Electrolytes

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Online electrochemical mass spectrometry (OEMS) was employed to investigate the behavior of ethylene carbonate (EC) and fluoroethylene carbonate (FEC) co-solvents in high voltage lithium-ion batteries based on high energy lithium nickel cobalt manganese oxide (HE-NCM) and SFG6 graphite (SFG6) electrodes. Gas evolution from HE-NCM and SFG6 electrodes was studied during two charge/discharge cycles in half-cell and full-cell configuration using electrolytes composed of 1 M LiPF6 in either 3:7 (w/w) EC:DEC or 3:7 (w/w) FEC:DEC. The results suggest that some CO2 formation is caused by reactive oxygen species originating from Li2MnO3 domain activation. The electrolyte composition has no effect on O2 evolution during Li2MnO3 domain activation and oxidative CO2 evolution in HE-NCM/Li half-cells. In contrast, decomposition of PF6− is significantly enhanced in electrolyte containing FEC and found to be strongly facilitated by the SuperC65 conductive carbon additive employed in the HE-NCM electrodes. EC and FEC clearly follow different reductive decomposition pathways. This leads to major differences in solid electrolyte interphase (SEI) formation and affects follow-up reactions involving CO2 and possibly other processes relevant for the stability and endurance of high voltage lithium-ion batteries.

The overlithiated high energy nickel cobalt manganese oxide (HE-NCM, BASF SE), xLi2MnO3·(1−x)LiMO2 (M = Ni, Co or Mn, x ≈ 0.5), is an advanced positive electrode material with the prospect of ousting today’s state-of-the-art positive electrode materials for lithium-ion batteries (e.g. LiCoO2, LiNi1/3Co1/3Mn1/3O2, etc.) due to its high specific charge (≈250 mA h g−1) and operation potential (up to 4.7 V vs. Li+/Li). However, several challenges remain before a widespread commercialization is possible. For instance, gradual voltage and capacity fading occurs during cycling of HE-NCM, which is believed to be partly related to parasitic reactions occurring at the electrode/electrolyte interfaces and inside the electrolyte during battery cycling.

Online electrochemical mass spectrometry (OEMS) can provide unrivaled quantitative information on such interface reactions based on the analysis of gaseous electrolyte decomposition product formation during electrochemical cycling. In this context, the study of gas evolution differences arising from electrolyte additives/co-solvents such as fluoroethylene carbonate (FEC) and ethylene carbonate (EC) is of particular interest to understand the chemistry influencing electrochemical interface stability.

Lately, it has been reported in several independent studies that fluoroethylene carbonate (FEC) can have beneficial effects on the cycling behavior of diverse lithium-ion battery anode materials and cathodes. Experimental investigations suggest that these effects are due to the comparably high stability of fluorinated carbonates at high potentials and FEC’s specific reductive decomposition properties (reductive CO2 formation).

The aim of the study is to present OEMS investigations of O2, C2H4, CO2, and POF3 gas evolution from HE-NCM/SFG6 half- and full-cells during the first two galvanostatic charge/discharge cycles in EC:DEC and FEC:DEC based 1 M LiPF6 electrolytes. The impact of FEC and EC on overall gas evolution, Li2MnO3 domain activation, cathodic and anodic decomposition reactions, SEI formation, and PF6− stability is discussed. Furthermore, cell configuration effects and the role of SuperC65 conductive carbon additive in PF6− decomposition are addressed. Finally, a scheme of the major parasitic reactions and their interdependence in HE-NCM batteries is proposed.

**Experimental**

**Electrode preparation.**—HE-NCM electrodes were prepared from slurries containing 93 wt% HE-NCM material (BASF SE), 3 wt% polyvinylidene fluoride (PVDF, Kynar HSV 900, Arkema), 2.64 wt% Super C65 (Imerys), and 1.36 wt% graphite on SFG6 (Imerys) dispersed in N-methylpyrroliodine (NMP, Sigma-Aldrich). Celgard 2400 (Celgard) sheets were coated ~200 μm thick with slurry by doctor blading and dried for 8 hours under dynamic vacuum at 80°C. 12 mm diameter electrodes (approximate loading: 12 mg/cm2) were punched and further dried under dynamic vacuum at 80°C for ≥12 h prior to introduction into an argon filled glove box.

SFG6 electrodes were prepared from slurries containing 96.2 wt% SFG6 and 3.8 wt% PVDF dispersed in NMP. The slurries were coated ~200 μm thick onto Celgard 2400 sheets by doctor blading and dried for 8 hours under dynamic vacuum at 80°C. 20 mm diameter electrodes (approximate loading: 4 mg/cm2) were punched and dried further under dynamic vacuum at 80°C for ≥12 h prior to introduction into an argon filled glove box.

SuperC65 electrodes were prepared from slurries containing 79 wt% SuperC65 and 21 wt% PVDF dispersed in NMP. The slurries were coated ~200 μm thick onto Celgard 2400 sheets by doctor blading and dried for 8 hours under dynamic vacuum at 80°C. 18 mm diameter electrodes (approximate loading: 0.8 mg/cm2) were punched and dried further under dynamic vacuum at 80°C for ≥12 h prior to introduction into an argon filled glove box.

**Online electrochemical mass spectrometry (OEMS).**—A custom-made 2-electrode OEMS cell was employed and cell assembly was performed inside an argon filled glove box for all measurements. For cells in half-cell configuration 20 mm diameter disks of 0.75 mm thick lithium metal foil (Sigma-Aldrich) were used as counter electrodes. HE-NCM/SFG6 half-cells were analyzed in both possible configurations, with the SFG6 electrode positioned either at the top or at the bottom of the cell stack. 28 mm diameter Celgard 2400 disks, dried under dynamic vacuum at 80°C for ≥12 h prior to introduction into the glove box, were used as separators. As electrolyte, 100 μl ready-made mixtures of 1 M lithium hexafluorophosphate (LiPF6) in either 3:7 (w/w) ethylene carbonate (EC)/diethyl carbonate (DEC) or in 3:7 (w/w) fluoroethylene carbonate (FEC)/diethyl carbonate (DEC)
Figure 1. Galvanostatic OEMS. a) HE-NCM/Li half-cell in 1 M LiPF$_6$ 3:7 (w/w) EC:DEC, b) HE-NCM/Li half-cell in 1 M LiPF$_6$ 3:7 (w/w) FEC:DEC, c) HE-NCM/SFG6 full-cell in 1 M LiPF$_6$ 3:7 (w/w) EC:DEC, d) HE-NCM/SFG6 full-cell in 1 M LiPF$_6$ 3:7 (w/w) FEC:DEC (inset: magnified view of the HE-NCM related CO$_2$ formation during the first charge). The quantities in parentheses refer to the integrated gas amounts normalized with respect to the mass of the active material, respectively. The wide, solid lines in c) and d) are the sums of the gas evolution traces observed in the corresponding HE-NCM/Li and SFG6/Li half-cells. Temporal shifts between the full-cell and the sum-of-half-cell traces are due to slight deviations in electrochemical cycling behavior of the respective cells. Dashed vertical lines are included as guides to the eye and mark the beginnings of new electrochemical cycling stages. The hatchings in c) and d) highlight the parts of the measurement referred to as “reductive C$_2$H$_4$ and CO$_2$ evolution” (R) and “first oxidative CO$_2$ formation” (Ox$_1$) in the main text. The orange arrow in c) indicates the diminishment in CO$_2$ evolution discussed in the main text. Larger size versions of a) - d) can be found in the supporting information.

(BASF SE, water contents $\leq$ 20 ppm as verified by coulometric Karl-Fischer titration) were employed.

The OEMS setup comprised a quadrupole mass spectrometer (MS, QMS 200, Pfeiffer PrismaTM, Germany) for partial pressure measurements, a pressure transducer (PS, PAA-33X, Keller Druck AG, Switzerland) for cell pressure, temperature and internal volume determination, stainless steel gas pipes and Swagelok fittings (3 mm compression tube fittings, Swagelok, OH, US) for OEMS cell attachment, a set of solenoid valves (2-way magnetic valve, Series 99, silver-plated nickel seal, Parker, US) and a scroll pump (nXDS15i, EDWARDS GmbH, Germany) for efficient flushing. The magnetic valves were automatically opened/closed with a Solid State Relay Module (NI 9485 Measurement System, National Instruments, TX, US) connected to a computer with a home-made LabVIEW software (NI LabVIEW 2013, National Instruments, TX, US).

For partial pressure and gas evolution rate analysis 0.7 mL of gas were extracted from the headspace ($\sim$ 3.2 ml) of the cell and replaced by pure argon (quality 5.0). To enable quantitative comparability the partial pressures derived from the ion-currents at the MS detector were all normalized by the home-made LabView software with respect to the partial pressure of argon as determined from the ion-current at 36 m/z. Gas evolution rates were calculated in the same software. Before and after each measurement, the MS ion-current signals at 32 and 44 m/z were related to known concentrations of O$_2$ (1000 ppm) and CO$_2$ (200 ppm) using an argon-based calibration gas, enabling precise gas quantification for O$_2$ and CO$_2$. The time evolution of C$_2$H$_4$ (27 m/z), and POF$_3$ (85 m/z) was also recorded and allows direct semi-quantitative comparison between the evolution of these fragments from one data set to another. The indicated m/z channels were deliberately selected for monitoring the described molecular species because they provided the strongest and least obscured signals. Further m/z channels were monitored to ensure consistent temporal evolution of different fragments derived from the same molecular species.

Results and Discussion

Overall gas evolution.—Consistent with previous reports, Figures 1a and 1b show a substantial evolution of both CO$_2$ (44 and 28 m/z) and O$_2$ (32 m/z) during the two first charge/discharge cycles
of a HE-NCM/Li half-cell. An early CO₂ formation rate maximum occurs at ca. 4.2 V vs. Li⁺/Li and is accompanied by the onset of slow O₂ release related to Li₂MnO₃ domain activation. The major part of the O₂ originating from Li₂MnO₃ domain activation is, however, released along with a second CO₂ maximum at the end of the first charge when the potential reaches values >4.5 V. The latter CO₂ evolution is also observed in the following cycles in which, in contrast, the early CO₂ formation process and the O₂ release cease to occur. CO₂ formation is slightly enhanced in FEC:DEC compared to EC:DEC, particularly when the HE-NCM electrode is cycled below 3 V. Finally, the PF₆⁻ decomposition product POF₃ (85 m/z) evolves in a similar fashion as CO₂ while a slow and a rapid formation process are observed during the first charge at ∼4.5 V and at >4.5 V, respectively; only the latter process persists throughout the following cycles. Again, the extent of POF₃ formation is appreciably higher in FEC:DEC compared to EC:DEC.

In this context we would like to stress that water contents <20 ppm are guaranteed by the electrolyte supplier for both the EC:DEC and the FEC:DEC electrolytes. Furthermore, we do not see any indication of considerable H₂ evolution in the FEC electrolyte that would be expected to occur due to the reduction of water impurities on the Li electrode (data not shown). Consequently, we conclude that if differences in water content play a role in the increased CO₂ and POF₃ evolution in FEC:DEC, these differences fall into a low ppm range of concentrations that is not detectable by our instrumentation.

In summary, the overall gas evolution behavior observed by OEMS is astonishingly similar in HE-NCM/Li half-cells regardless of whether FEC:DEC or EC:DEC based electrolyte is employed and apparently defies the above mentioned literature reports about marked differences in the electrochemical properties of FEC.

**Reductive C₂H₄ and CO₂ evolution.**—Figures 1c and 1d show the corresponding OEMS results for HE-NCM/SFG6 full-cells with EC:DEC and FEC:DEC based electrolytes, respectively. These results clearly show that there is a major, co-solvent dependent difference in the gas evolution in the full-cells: with EC:DEC electrolyte, substantial amounts of C₂H₄ and no CO₂ are evolving during the very early stages of the first charge (hatched area R in Figure 1c). The situation is the exact opposite with FEC:DEC electrolyte, where substantial additional CO₂ but hardly any C₂H₄ are evolving during the corresponding phase of the measurement (hatched area R in Figure 1d). Based on OEMS measurements of SFG6/Li half-cells (Figures S1c, d), these additional C₂H₄ (EC:DEC) and CO₂ (FEC:DEC) evolution features observed at the beginning of the first charge in the full-cell configuration (hatched areas R in Figures 1c, 1d) can be attributed to reductive EC and FEC decomposition, respectively. This assignment is corroborated by a comparison of the full-cell gas evolution traces (thin lines with small squares in Figures 1c, 1d) with the sum of HE-NCM/Li and SFG6/Li half-cell traces (wide, solid lines in Figures 1c, 1d). Both the formation rates and the integrated gas amounts of the full-cells agree well with the sums of the corresponding half-cells during the very early stages of the first charge. The underlying C₂H₄ and CO₂ formation processes are consequently mostly due to reductive electrolyte decomposition and are unaffected by the respective positive electrodes. The broadening of the reductive C₂H₄ and CO₂ peaks in the full-cells compared to the half-cells can be rationalized by differences in cell configuration: Sampling occurs at the top of the cell so that gases formed at the SFG6 electrode located at the bottom of the full-cell need to diffuse through the separator and the HE-NCM electrode in order to be detected. This is not the case in the SFG6/Li half-cells, where the SFG6 electrode is positioned at the top, in close proximity to the gas head-space. Analogously, the oxidative CO₂ and O₂ peaks are not broadened in the full-cells, because the corresponding formation processes take place at the HE-NCM electrode, which is located at the top in both HE-NCM/Li half- and full-cells. In fact, upon interchanging the positions of the HE-NCM and SFG6 electrodes in the full-cells, the evolution traces of the gases formed at or close to the HE-NCM electrode, are affected considerably (Figure 2, Figure S1, Figure S2).

Thorough inspection of Figure 1a and Figure 1b shows that CO₂ formation due to reductive FEC decomposition not only results in major differences between the full-cells, but also explains the more unobtrusive differences in CO₂ formation in the HE-NCM/Li half-cells. In EC:DEC a small additional CO₂ “spike” is apparent at the very beginning of the second charge, indicative of the oxidation of (inorganic and/or organic) lithium carbonate species formed on the HE-NCM electrode during the preceding discharge. In contrast, CO₂ formation actually starts already at the end of discharge with FEC:DEC. This is because the potential of the HE-NCM electrode reaches values <2.9 V at this stage which is sufficient for reductive FEC decomposition to set in, as also apparent from Figure S1d in the supporting information.
Oxidative CO2 evolution.—While there is good agreement between oxidative CO2 formation in the FEC:DEC full- and half-cells as well as in the EC:DEC half-cell (Figures 1a, 1b, 1d), the first oxidative CO2 formation process (Figure 1c, hatched area Ox1) is considerably diminished in the EC:DEC full-cell (Figure 1c, orange arrow).

We suppose that these observations can be explained in the following way: CO2 formed at the HE-NCM electrode can migrate to and become reduced at the counter electrode in considerable quantities provided that (1) the surface area of the counter electrode is sufficiently large and (2) the counter electrode is not covered by a passivating SEI layer before the CO2 arrives there. Both of these criteria are only met simultaneously in case of the EC:DEC full-cell because SFG6 has a sufficiently large electrochemically active surface area and SEI formation has not yet reached completion by the end of the first half of the first charge in the EC:DEC electrolyte. In contrast, no reductive consumption of CO2 is observed with the other cells because (1) the surface area of the half-cell lithium metal counter electrodes (Figure 1a, 1b) contact with electrolyte is much smaller compared to the full-cell SFG6 counter electrode and (2) an effective SEI layer is obtained much earlier in the FEC:DEC full-cell (Figure 1d) due to the very early CO2 releasing reductive FEC decomposition.

Li2MnO3 domain activation and O2 evolution.—O2 formation is negligibly affected by the choice of electrolyte and counter electrode (Figure 1). The fact that it takes place only during the first charge in all HE-NCM half- and full-cells investigated clearly indicates that Li2MnO3 domain activation is its major cause. In agreement with computational work by Xiao et al.,47 O2 is observed to evolve very slowly throughout the major part of the 4.5 V plateau and rapid O2 release only occurs at the very end of the first charge when the extent of Li2MnO3 delithiation has become sufficient for O2 release to occur spontaneously. Taking previous work by Sathiya et al.45,46 and Castel et al.6 into account, we propose in summary that when HE-NCM is being charged, reversible formation of peroxy-species, (O2)2*- takes place in the layered LiMO2 (M = Ni, Co, or Mn) whereas the concomitant Li2MnO3 domain activation involves a significant extent of (irreversible) (O2)2* release from the lattice. The resulting adsorbed and dissolved reactive oxygen species lead to (1) chemical decompositions of electrode components, solvent, or the electrolyte salt as well as (2) electrochemical O2 formation, thus explaining not only the early oxidative CO2 formation and the O2 evolution at >4.5 V, respectively, but also the disappearance of both of these processes in later cycles in which no reactive oxygen species are available anymore because all Li2MnO3 domains have already been activated.

POF3 evolution.—POF3 is formed in all HE-NCM full- and half-cells (Figures 1a and 1b, Figure 2a, Figure S1, Figure S2), but is not observed in any of the SFG6/Li half-cells, regardless of electrolyte (Figures S1c, d), which suggests that the HE-NCM electrode—in combination with anodic polarization—is required for the hydrolysis of the salt. The fact that the POF3 traces are strongly affected by inverting the full-cell configuration, further corroborates this hypothesis (Figure 2). However, POF3 formation also occurs in SuperC65/Li half-cells (Figure 3b) and thus does not depend on the presence of HE-NCM itself or the availability of reactive oxygen species. In fact, a quantitative comparison between HE-NCM/Li and SuperC65/Li half-cells in EC:DEC based electrolyte reveals that POF3 formation is substantially facilitated by SuperC65, which is used as a conductive additive in the HE-NCM electrodes. While the BET electrode surface area differs only by a factor of approximately 5 between the HE-NCM and the SuperC65 electrode, the maximum POF3 formation rate and the total amount of POF3 normalized with respect to the corresponding BET electrode surface areas are enhanced by factors of 9.5 in rate and >19 in amount, respectively, with the SuperC65 electrode (Table 1). The latter finding suggests that POF3 formation is strongly dependent on specific interactions with SuperC65 carbon.

The observation of distorted POF3 traces in both HE-NCM (bottom)/SFG6 (top) full-cells (Figure S2) and in the strongly POF3

Table 1. SuperC65 carbon facilitated POF3 formation.

|          | BET surface area1 | Max. POF3 formation rate | Total POF3 amount |
|----------|-------------------|--------------------------|------------------|
| HE-NCM electrode | 11.8 m² g[HE-NCM]−1 | 250 nmol m² | 250 nmol m² |
| SuperC65 electrode | 63 m² g[SuperC65]−1 | 23.7 nmol m² | >4760 nmol m² |
| Ratio    | 5.3               | 9.5                      | >19.0            |

1see supporting information for details about calculation.

Figure 3. Cyclic voltammogram of HE-NCM/Li (a) and SuperC65/Li (b) half-cells in 3:7 (w/w) EC:DEC based 1 M LiPF6 electrolyte. The approximate evolution rates were normalized with respect to the corresponding BET electrode surface areas (see supporting information for details). In addition, the non-calibrated integrated POF3 gas amounts are provided. The respective active material used for normalization is indicated in brackets.
evolving SuperC65/Li half-cell (Figure 3b) is indicative of poorly soluble, gaseous reactants being involved in POF3 formation. Trapped gas bubbles lead to increased time-of-residence for reactants in direct contact with electrolyte and could explain both peak broadening and an overall increase in POF3 formation. Furthermore, a certain extent of randomness is expected for the release of gases from trapped bubbles, which is in good agreement with the somewhat stochastic behavior of POF3 formation under these conditions. An obvious candidate for such a reactant is PF3, which is a gas at room temperature and a potential POF3 precursor.

The reasons for why POF3 formation is enhanced by FEC remain debatable. The reactions

\[
\text{Li}_2\text{CO}_3 + \text{LiPF}_6 \rightarrow 3\text{LiF}^+ + \text{POF}_3 + \text{CO}_2 \quad [1]
\]

and

\[
\text{Li}_2\text{CO}_3 + \text{PF}_3 \rightarrow 2\text{LiF}^+ + \text{POF}_3 + \text{CO}_2 \quad [2]
\]

have been proposed in the literature.47 Based on these reactions, increased POF3 (and CO2) formation could be explained by higher amounts of Li2CO3 inside the FEC:DEC electrolyte. This would obviously require either the availability or the solubility of Li2CO3 to be enhanced in FEC:DEC compared to EC:DEC electrolyte. The HE-NCM/SFG6 full-cell results (Figures 1c and 1d, Figures S1e and f) on their own would suggest that the decisive parameter is the availability of Li2CO3, since this quantity is likely to be substantially higher in FEC:DEC electrolyte because of the substantial additional amounts of CO2 originating from reductive FEC decomposition on the SFG6 counter electrode that can easily be converted to Li2CO3. However, POF3 formation is enhanced to almost the same extent by FEC:DEC in the HE-NCM/Li half-cell, even though the co-solvent dependent difference in CO2 evolution is only minor between the respective half-cells (Figures 1a and 1b). Two (complementary) explanations can resolve this apparent contradiction: (1) There are co-solvent dependent differences in Li2CO3 solubility and/or (2) there is another source of Li2CO3 that is independent of the CO2 evolved during cycling.

With respect to explanation 1, it appears that any solubility differences would have to be related to differences in solvent polarity rather than specific solvent ··· Li2CO3 interactions, for the simple reason that EC and FEC are structurally so similar to each other. Interestingly, Kawamura et al.48 suppose that solvent polarity may affect the equilibria

\[
\text{LiPF}_6 \leftrightarrow \text{Li}^+ + \text{PF}_6^- \quad [3]
\]

\[
\text{LiF}^- \leftrightarrow \text{Li}^+ + \text{PF}_3 \quad [4]
\]

in such a way that the non-ionic dissociation path 4 is facilitated by low dielectric constant solvents, leading to increased levels of LiPF3 decomposition caused by the instability of PF3. Unfortunately, there is a lack of reliable literature data about dielectric constants for FEC, EC, DEC, and – in particular – for binary mixtures of these, determined under comparable experimental conditions.49,50 Therefore, it is difficult to judge if and to which extent reactions 1–4 are relevant for the observed differences. If FEC:DEC were more polar than EC:DEC, the enhanced POF3 formation in FEC:DEC based electrolyte would have to be interpreted in such a way that the major effect of solvent polarity is to increase Li2CO3 solubility thus facilitating decomposition reactions 1 and 2 and outcompeting stabilization effects arising from equilibrium 3. In the case of FEC:DEC electrolyte being less polar than EC:DEC, the differences in POF3 formation would suggest dominance of destabilization via equilibrium 4 over the decrease in decomposition via reactions 1 and 2 due to lower Li2CO3 solubility. Since according to this line of argument both higher and lower solvent polarity can explain enhanced PF6– decomposition it remains an open question which effect actually is prevailing.

Regarding explanation 2, it is important to realize that most NCM materials contain considerable amounts of Li2CO3 and LiOH impurities. Even though a detailed investigation of the effects of these impurities on cell performance and gas evolution is out of the scope of this work, we would still like to address two potentially important implications of the presence of such impurities for the POF3 and CO2 evolution discussed here and further above:

(1) Provided that they are present in sufficient quantities, these impurities could contribute substantially to the overall evolution of POF3 and CO2 via Equations 1 and 2 in both half- and full-cells.

(2) The fact that the amount of these impurities (with respect to the mass of the active material) has to be the same in all cells, regardless of the choice of co-solvent, would further imply that the solubility of Li2CO3 were indeed slightly higher in FEC:DEC compared to EC:DEC because otherwise the FEC dependent POF3 evolution enhancement in the half-cells could not be explained.

Summary.—Electrochemical cycling of HE-NCM can be subdivided into the following three phases to facilitate an integrated discussion of the processes described above:

(1) Initial stage of first charge (<4.5 V).

(2) Final stage of first charge (>4.5 V).

(3) First discharge and subsequent cycles.

Phase (1) comprises the formation of a solid electrolyte interphase (SEI) on the SFG6 counter electrode and Li2MnO3 domain activation inside the HE-NCM electrode. SEI formation is attended by reductive solvent decomposition with C2H4 and CO2 as the major gaseous products in EC:DEC and FEC:DEC, respectively. Li2MnO3 domain activation entails the release of comparably small quantities of O2 as well as the evolution of substantial amounts of CO2 that are likely to arise from reactive oxygen mediated decomposition reactions (Scheme 1a). As long as reactive oxygen species or other reactive intermediates are available in sufficient quantities, self-sustaining decomposition cycles resulting in further decomposition products such as POF3 can occur. These are kept at bay by the conversion of reactive intermediates to non-reactive species e.g. via polymerization or reduction on the negative electrode. The ability of the negative electrode to scavenge reactive intermediates differs markedly between the EC:DEC and the FEC:DEC based electrolyte during this phase. Due to the reductive FEC decomposition that sets in at very positive potentials and is accompanied by the evolution of substantial quantities of CO2, the SEI forms much earlier and presumably contains a considerably larger fraction of inorganic components such as Li2CO3 in FEC:DEC than in EC:DEC based electrolyte.

At the onset of phase (2), a critical level of Li2MnO3 domain activation is reached so that the electrode potential continues to increase beyond 4.5 V, and O2 rather than reactive oxygen is released from the HE-NCM electrode during the activation of remaining Li2MnO3 domains (Scheme 1b). The potentials are now sufficiently high for direct solvent and electrolyte oxidation on the HE-NCM electrode to set in, resulting in rapid evolution of CO2 and POF3. Considering the effect of SuperC65 carbon on the oxidative decomposition of LiPF6, it is possible that the rapid CO2 evolution is to a large extent due to carbon corrosion reactions.

Phase (3) is characterized by its consistent cycling and gas evolution behavior that deviates from the behavior during the first charge. Some reduced decomposition products such as Li2CO3 are formed during discharge and give rise to a small oxidative CO2 “spike” at the beginning of the ensuing charge. This “spike” is considerably enhanced in FEC:DEC based electrolyte by CO2 originating from reductive FEC decomposition which, in fact, already sets in at the end of discharge. From the second cycle onwards all Li2MnO3 domains are expected to be active so that the formation of reactive oxygen species, CO2 and POF3 during charging at potentials <4.5 V ceases and O2 formation at the end of charge becomes marginal. In contrast, the CO2 and POF3 evolving processes at potentials >4.5 V persist.
While HE-NCM/Li half-cells show hardly any difference between EC:DEC and FEC:DEC based electrolytes with respect to the overall gas evolution, integrated investigations of half- and full-cells reveal electrolyte-effects that are highly relevant for real batteries.

Substantial differences in the cathodic decomposition of FEC processes while thin arrows indicate coupled chemical reactions.

Conclusions

(1) While HE-NCM/Li half-cells show hardly any difference between EC:DEC and FEC:DEC based electrolytes with respect to the overall gas evolution, integrated investigations of half- and full-cells reveal electrolyte-effects that are highly relevant for real batteries.

(2) Substantial differences in the cathodic decomposition of FEC compared to EC will have a major impact on SEI formation kinetics and composition. In FEC:DEC based electrolyte the SEI can form earlier and will contain a substantially larger fraction of inorganic components such as Li2CO3.

(3) The disappearance of early anodic CO2 evolution after the first charge/discharge cycle provides indirect experimental evidence for the formation of reactive oxygen species during Li2MnO3 domain activation. Even though no direct electrolyte dependence is observed for the underlying processes, follow-up reactions with a major impact on battery performance and endurance might be electrolyte dependent.

(4) PF6− decomposition is facilitated by the SuperC65 conductive carbon additive in the HE-NCM electrodes and is enhanced in FEC:DEC compared to EC:DEC based electrolyte.

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