

# The Effect of Electrolyte Additives upon the Lithium Kinetics of Li-Ion Cells Containing MCMB and $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ Electrodes and Exposed to High Temperatures

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With the intent of improving the performance of lithium-ion cells at high temperatures, we have investigated the use of a number of electrolyte additives in experimental MCMB-  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cells, which were exposed to temperatures as high as 80°C. In the present work, we have evaluated the use of a number of additives, namely vinylene carbonate (VC), dimethyl acetamide (DMAc), and mono-fluoroethylene carbonate (FEC), in an electrolyte solution anticipated to perform well at warm temperature (i.e., 1.0M  $\text{LiPF}_6$  in EC+EMC (50:50 v/v %). In addition, we have explored the use of novel electrolyte additives, namely lithium oxalate and lithium tetraborate. In addition to determining the capacity and power losses at various temperatures sustained as a result of high temperature cycling (cycling performed at 60° and 80°C), the three-electrode MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cells (lithium reference) enabled us to study the impact of high temperature storage upon the solid electrolyte interphase (SEI) film characteristics on carbon anodes (MCMB-based materials), metal oxide cathodes, and the subsequent impact upon electrode kinetics.

## Introduction

There is continued interest to improve the high temperature resilience of Li-Ion cells, due to the presence of degradation processes which lead to irreversible capacity loss and impedance growth resulting in power fade. It is generally acknowledged that, regardless of the electrode chemistries, the electrolyte solution can significantly participate in these degradation mechanisms. This has prompted studies that have focused upon the reactivity of lithium-ion based electrolyte solutions. For example, it has been established that  $\text{LiPF}_6$  can thermally decompose to form LiF and  $\text{PF}_5$ , the later product being a strong Lewis acid which further reacts with alkyl carbonates in solution to form a number of byproducts, including  $\text{CO}_2$ , alkyl ethers ( $\text{R}_2\text{O}$ ), alkylfluorides, phosphorus oxyfluoride ( $\text{OPF}_3$ ) and fluorophosphates ( $\text{OPF}_2\text{OR}$ ,  $\text{OPF}(\text{OR})_2$ ).<sup>1,2</sup> From this and other studies, it has been concluded that the electrolyte type plays a key role in

establishing the relative resilience to high temperature exposure and has spurred research in this area.

To improve the high temperature resilience of lithium-ion cells by modifying the electrolyte formulation, a number of approaches can be taken, including: (a) optimizing the solvent blends, (b) using novel co-solvents, (c) using novel electrolyte salts, or (d) utilizing electrolyte additives. With regard to the last approach, vinylene carbonate (VC) has been reported to be an effective additive in improving the high temperature cycle life and storage characteristics.<sup>3,4</sup> The mechanism by which VC imparts improved stability to the cell is that it is believed to be sacrificially polymerized on the electrode surfaces during the formation process, producing protective films which prevent further electrolyte reaction at the interface. In an attempt to minimize the thermal decomposition of the  $\text{LiPF}_6$  electrolyte salt, Lucht and coworkers have investigated using Lewis base electrolyte additives<sup>5</sup>, such as dimethyl acetamide (DMAC) and N-methyl pyrrolidinone (NMP), as stabilizing agents which have been found to reversibly bind with  $\text{PF}_5$ , preventing  $\text{LiPF}_6$  and carbonate solvents from decomposition at high temperatures. In collaboration with URI, we have demonstrated good performance of 1.0 M  $\text{LiPF}_6$  EC+DEC+DMC (1:1:1 v/v %) solutions with these additives after being subjected to high temperature storage.<sup>6</sup> Mono-fluoroethylene carbonate has been investigated in electrolyte solutions consisting of FEC+EC+PC (1:3.5:3.5) primarily to prevent the exfoliation of graphite anode electrodes when used in the presence of propylene carbonate (PC),<sup>7</sup> and we envisioned that this additive could assist in the formation of robust SEI layers.

In the present work, we have evaluated the use of these additives, namely vinylene carbonate (VC), dimethyl acetamide (DMAC), and mono-fluoroethylene carbonate (FEC), in an electrolyte solutions anticipated to perform well at warm temperature (i.e., 1.0M  $\text{LiPF}_6$  in EC+EMC (50:50 v/v %)). In addition, we have explored the use of novel electrolyte additives, namely lithium oxalate and lithium tetraborate, as shown in Fig. 1. Lithium oxalate was envisioned to complex any free  $\text{PF}_5$  generated from the decomposition of  $\text{LiPF}_6$  much in the same manner as  $\text{LiBOB}$  has been reported to stabilize  $\text{LiPF}_6$ -based solutions.<sup>8</sup>

In addition to determining the capacity and power losses at various temperatures sustained as a result of high temperature cycling (cycling performed at 60° and 80°C) the three-electrode MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cells (with lithium reference), enabled us to study the impact of high temperature storage upon the solid electrolyte interphase (SEI) film characteristics on carbon anodes (MCMB-based materials), metal oxide cathodes, and the subsequent impact upon electrode kinetics. In order to investigate these issues, a number of electrochemical characterization techniques were employed including: DC Tafel and micro (or linear) polarization, and electrochemical impedance spectroscopy (EIS). All of these techniques were performed before and after each storage period,

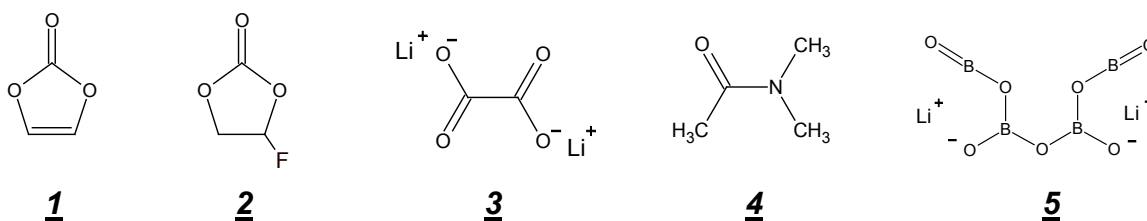


Figure 1. Various additives selected for incorporation into multi-component carbonate electrolyte solutions for investigation in MCMB- $\text{LiNiCoO}_2$  cells at high temperature, including vinylene carbonate (VC), **1**, mono-fluoroethylene carbonate (FEC), **2**, lithium oxalate, **3**, dimethyl acetamide (DMAC), **4**, and lithium tetraborate (LTB), **5**.

## Experimental

For detailed electrical and electrochemical measurements, three-electrode, O-ring sealed, glass cells were employed, which consisted of spiral rolls of MCMB (1028)-carbon anodes,  $\text{LiNi}_{0.80}\text{Co}_{0.2}\text{O}_2$  cathodes, and lithium reference electrodes separated by porous polypropylene (Tonen-Setella). The carbonate-based electrolytes, consisting of lithium hexafluorophosphate,  $\text{LiPF}_6$ , dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC), were purchased from Ferro Corp. (now referred to as Novolyte Technologies, Inc.) with less than 50 ppm of water (battery grade). The electrolytes evaluated in this study include: (a) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) (baseline electrolyte), (b) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 2.0 % vinylene carbonate (VC), (c) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 2.0 % VC + 2% dimethyl acetamide (DMAc), (d) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 2.0 % mono-fluoroethylene carbonate (FEC), (e) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 4.0 % FEC, (f) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + lithium oxalate, and (g) 1.0 M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 2.0% lithium tetraborate (LTO).

The cycling tests and charge-discharge measurements were performed with an Arbin battery cycler. These tests were typically done at current densities of  $0.25 \text{ mA/cm}^2$  ( $\sim C/12$  rate) and  $0.50 \text{ mA/cm}^2$  ( $\sim C/6$  rate) for charge and discharge, respectively. The cells were charged to 4.10V, followed by a tapered charge period, where the current is allowed to decay to a C/100 rate, and discharged to 2.75V, with 15 minute rest periods between the charge/discharge steps. Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 Frequency Response Analyzer was used with this potentiostat for impedance measurements, with M388 software.

## Results and Discussion

### Experimental Cell Results

Formation Characteristics. Prior to electrochemical characterization, the cells were subjected to formation cycling, which consisted of performing five cycles over a voltage range of 2.75 to 4.10 using  $\sim C/16$  charge and discharge rates. As illustrated in Table 1, all of the cells displayed very comparable behavior in terms of the coulombic efficiency (i.e., 84 to 87% for the first cycling and 97 to 98% on the fifth cycle). Some differences were observed in terms of the reversible capacity, which is in part due to variations in the electrolyte type, but is mainly attributable to cell to cell variations in the electrode weights. Of the electrolyte additives investigated, the use of mono-fluoroethylene carbonate resulted in the highest efficiencies and lowest cumulative irreversible capacity loss observed over the first five cycles.

Table 1. The reversible capacity (Ah) at 20°C of MCMB-LiNiCoO<sub>2</sub> cells containing electrolytes with and without various additives after storage at 55°C.

Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreversible Capacity (1st Cycle)	Coulombic Efficiency (1st Cycle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreversible Capacity (1st-5th Cycle)	Coulombic Efficiency (5th Cycle)
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %)	0.4664	0.4049	0.062	86.81	0.4014	0.3931	0.1006	97.93
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %) + 2% lithium oxalate	0.5055	0.4389	0.067	86.83	0.4333	0.4247	0.1162	98.01
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %) + 2% VC	0.4562	0.3862	0.070	84.66	0.3823	0.3753	0.1076	98.15
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %) + 2% VC + 2% DMAc	0.4429	0.3724	0.071	84.08	0.3740	0.3646	0.1167	97.48
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %) + 2% FEC	0.4980	0.4309	0.067	86.53	0.4129	0.4069	0.1040	98.55
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %) + 4% FEC	0.4906	0.4254	0.065	86.71	0.4240	0.4171	0.0950	98.37
1.0 M LiPF <sub>6</sub> EC+EMC (50:50 v/v %) + 2% LTB	0.4969	0.4272	0.070	85.97	0.4242	0.4144	0.1211	97.70

Discharge Characteristics After Exposure to High Temperature. To evaluate the effect of the electrolyte type upon the high temperature resilience, the experimental cells were subjected to period of cycling (20 cycle increments) at increasingly higher temperatures (i.e., at 60°C and 80°C). In total, 60 cycles were performed on the cells at high temperatures, including 20 cycles at 60°C and 40 cycles at 80°C. After every 20 cycles, the cells were subjected to characterization cycling, which included determining the rate capability at different temperatures (i.e., at 0° and 20°C). These tests involved discharging the cells using three different current levels (e.g., 25 mA, 50mA and 100 mA, corresponding to ~ C/16, C/8 and C/4 discharge rates), and allows not only the determination of the reversible capacity after being subjected to high temperature cycling, but also allows for the assessment of the power fade sustained by the cells, and the associated impedance build up. As illustrated in Fig. 2, all of the cells displayed rapid capacity decline, especially when cycled at the higher temperature (i.e., 80°C). Of the permutations evaluated, the cells containing the electrolytes containing VC and lithium oxalate as additive were observed to retain the greatest percentage of the initial capacity, as shown in Fig. 3. It should be noted that, in general, more rapid capacity fade is observed with these types of experimental cells, due to their flooded design and lack of hermiticity. In contrast, prototype cells manufactured by a battery vendor have been observed to have much better life characteristics. However, the trends displayed in the experimental cells can be extrapolated will to larger, hermitically sealed cells, based upon previous studies.

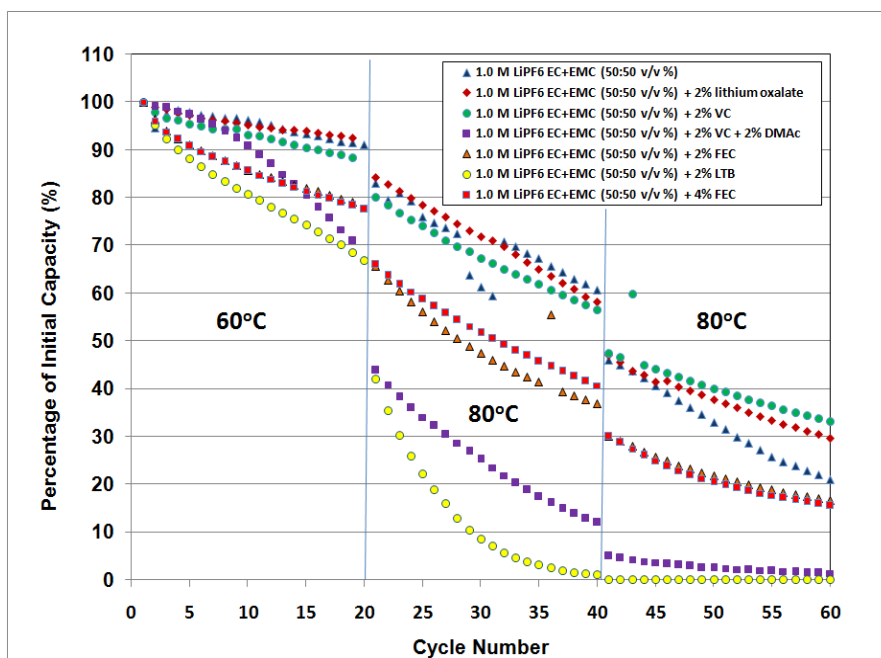


Figure 2. The cycle life performance at high temperatures (60° and 80°C) of MCMB-LiNiCoO<sub>2</sub> cells containing electrolytes with and without various additives.

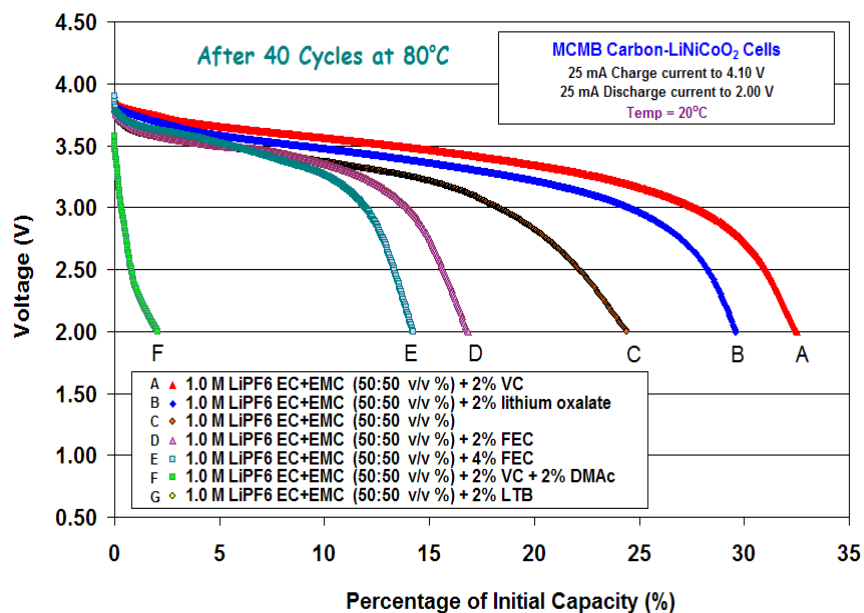


Figure 3. The reversible capacity (Ah) at 20°C of MCMB-LiNiCoO<sub>2</sub> cells containing electrolytes with and without various additives after being subjected to cycling at high temperature (60° and 80°C) for a total of 60 cycles.

In addition to determining the reversible capacity losses observed as a result of cycling at high temperature storage, the use of the experimental MCMB-Li<sub>x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> cells equipped with reference electrodes enabled us to study the effect of high temperature upon the solid electrolyte interphase (SEI) film characteristics on both electrodes, and the subsequent impact upon electrode kinetics. In order to investigate these issues, a number of electrochemical characterization techniques were employed including: DC Tafel and micro (or linear) polarization, and electrochemical impedance spectroscopy (EIS). These techniques were performed before and after completing each increment of 20 cycles at high temperatures.

### Electrochemical Impedance Spectroscopy (EIS) Measurements.

When performing Electrochemical Impedance Spectroscopy (EIS) measurements on most Li-ion cell chemistries and designs, it is generally observed that the interfacial impedance of the cathode (at low frequencies) dominates that of the anode in contributing to the overall cell impedance. This trend has consistently been observed with electrodes similar to the ones investigated in this study, with little impact arising from the type of electrolyte employed provided relatively stable, traditional systems are employed. The dominance of the contribution of the cathode to the cell impedance has also been observed by others, and is supported by other electrochemical characterization techniques, such as DC polarization studies, in which the carbonaceous anode can typically sustain much higher current densities and displays lower polarization effects. This is partly attributable to the corresponding cathode/anode active material balance.

Prior to initiating the cycling tests at high temperature, the electrochemical impedance behavior of the cathodes in contact with the various electrolytes was measured, as illustrated in Fig. 4. All data were generated at ambient temperature and open circuit voltages, corresponding to a state of charge of 100%, over a frequency range of 10<sup>5</sup> Hz to ~ 5 mHz, with ten data points taken over each decade. The impedance pattern obtained typically contains two relaxation loops, one at high frequency in the range of 10<sup>5</sup> to 10<sup>2</sup> Hz and the other in the low frequency (10<sup>2</sup> to 10<sup>-1</sup> Hz) range. The equivalent circuit typically used to interpret such an impedance pattern generally consists of a series resistance,  $R_s$ , which represents an algebraic sum of the electronic resistance from both the electrodes, leads and the electrolyte ionic resistance, a parallel resistor-capacitor network ( $C_{hf}$  and  $R_{hf}$ ) corresponding to the SEI characteristics in series for the high frequency relaxation loop, another resistor-capacitor parallel network in series for the low frequency relaxation loop ( $C_{lf}$  and  $R_{lf}$ ) to represent the electrode intercalation kinetics and a Warburg impedance ( $w$ ), to represent a slow solid state diffusion of lithium inside the cathode or anode.

As shown in Fig. 6, the cells containing electrolytes that possessed the addition of mono-fluoroethylene carbonate (both 2% and 4%) displayed much lower film and charge transfer resistances compared with the baseline formulation. In contrast, cells which contained 2% VC, 2% VC+2% DMAc, as well 2% LTB, as electrolyte additives all exhibited much higher film and charge transfer resistances, suggesting that these compounds react at the electrode interface and form a tenacious film that would impede the facile transport of lithium ions.

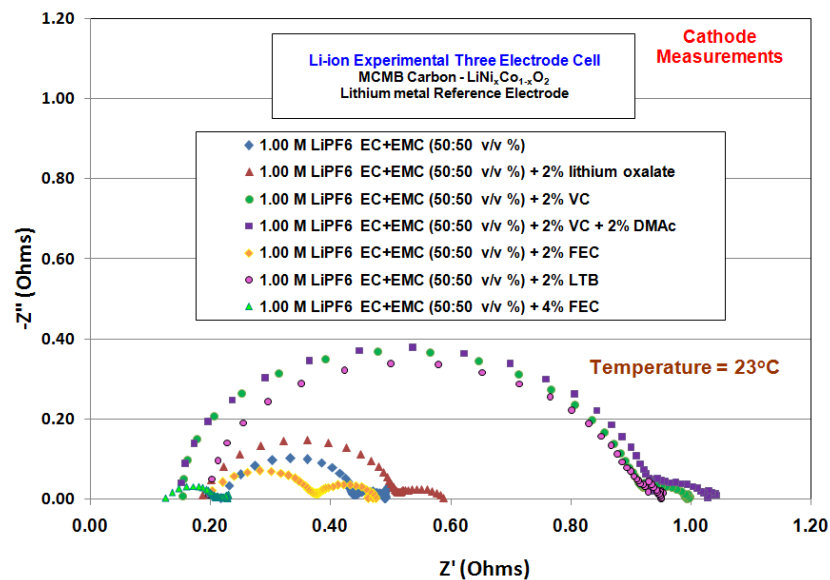


Figure 4. AC impedance (Nyquist) plots of  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  electrodes in MCMB- $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  cells containing 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) electrolyte with and without additives after formation cycling.

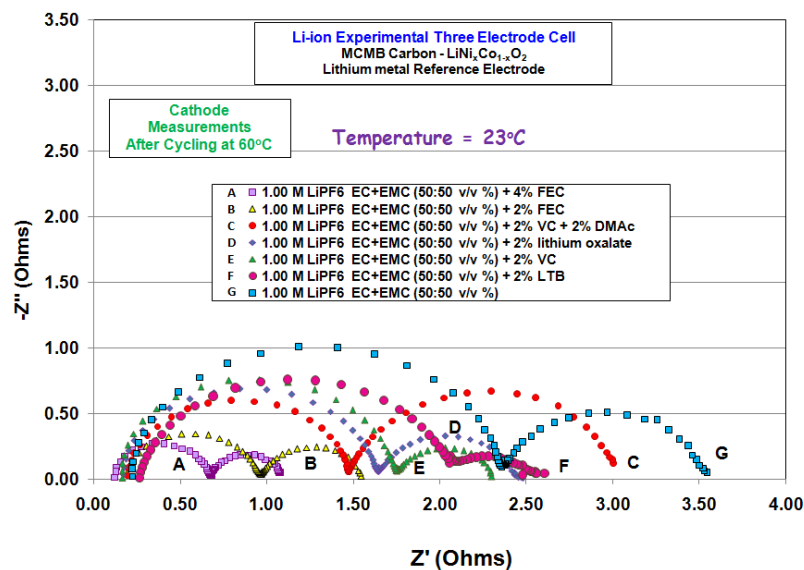


Figure 5. AC impedance (Nyquist) plots of  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  electrodes in MCMB- $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  cells containing 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) electrolyte with and without additives after being subjected to 20 cycles at 60°C.

After completing 20 cycles at 60°C, the EIS measurements were repeated on the  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  electrodes, as shown in Fig. 5. As illustrated, all of the electrolytes containing the additives under evaluation were observed to provide a beneficial effect in terms of preserving low film and charge transfer resistances. The following trend was observed, expressed in terms of increasing impedance: 4% FEC < 2% FEC < 2% VC + 2% DMAc < lithium oxalate < 2% VC < baseline electrolyte (no additive). The most dramatic effect was provided by the addition of mono-fluoroethylene carbonate, which appears to provide a protective surface coating at the electrode interface, preventing excessive electrolyte oxidation and/or film build (i.e., possibly involving a polymerization reaction similar to that postulated for ethylene carbonate). It is also evident that higher concentrations of the FEC appeared to have more of a beneficial effect, suggesting that the concentration of FEC can be further optimized. It also should be mentioned that in the cell containing the electrolyte with VC+DMAc, the film resistance was slightly lower than that of the baseline solutions, whereas as the charge transfer resistance was the largest of the group. The intention of using both of these additives together was based upon the notion that they would improve the high temperature resilience through different mechanisms (i.e., the VC is anticipated to produce robust SEI films, whereas the DMAc was envisioned to complex any free  $\text{PF}_6$ , thus limiting the thermal decomposition of the electrolyte salt).<sup>6</sup> From a comparison with results from a cell containing only VC as an additive, it is suggested that the DMAc imparts a deleterious effect upon the charge transfer resistance of the cathode upon being subjected to high temperatures.

When EIS measurements were performed on the MCMB anodes after the formation cycling and before exposure to high temperatures, it is apparent that there is less differentiation between the spectra obtained as a function of electrolyte type, as illustrated in Fig. 6. However, the cells containing the electrolytes 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) +2% FEC, 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + lithium oxalate, and 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 2% lithium tetraborate displayed lower film and charge transfer resistance compared with the baseline solution. In contrast, the cells containing the electrolytes with the different additive combinations were relatively comparable with the baseline solutions. When the EIS measurements were repeated on the MCMB anodes after high temperature cycling, as shown in Fig. 7, all of the cells appeared to preserve relatively low impedance characteristics in contrast to the behavior observed with the cathode measurements. In part, this can be attributed to the fact the selection of the baseline core electrolyte possesses a large proportion of ethylene carbonate content (i.e., 50% by volume), which has been reported to produce robust SEI films on carbon-based anodes and to possess good resilience to high temperatures.<sup>6</sup> Of the samples investigated, the cell containing the 2% VC as the electrolyte additive displayed the best performance, with the lowest series resistance ( $R_s$ ), and well as film ( $R_f$ ) and charge transfer resistances ( $R_{ct}$ ). This observation supports the numerous reports which have highlighted the beneficial effect that VC has upon the SEI characteristics of carbon anodes, especially when subjected to high temperatures. In addition to VC, the use of lithium oxalate appears to have a beneficial effect upon the nature of the MCMB SEI characteristics, although the nature of the mechanism that it imparts this beneficial effect is still unknown.



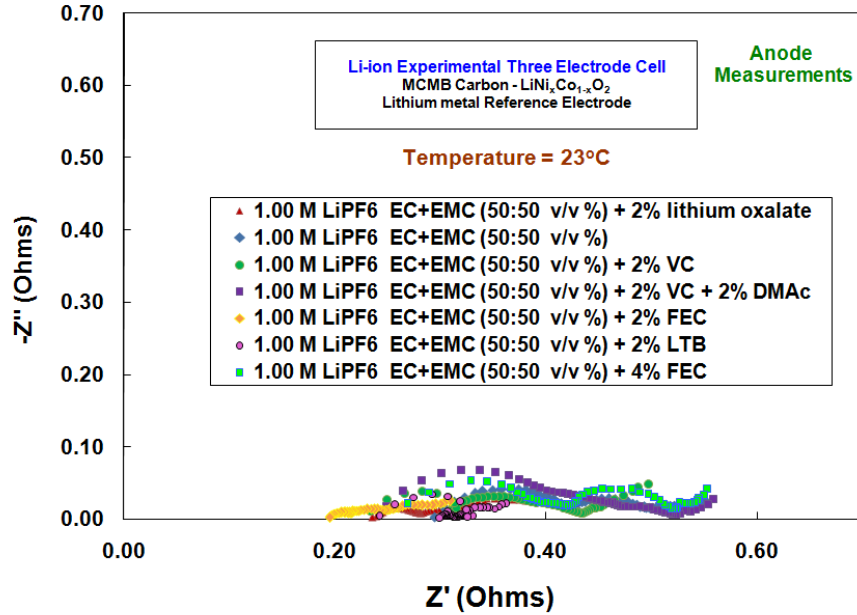


Figure 6. AC impedance (Nyquist) plots of MCMB electrodes in MCMB-LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> cells containing 1.0M LiPF<sub>6</sub> EC+EMC (50:50 v/v %) electrolyte with and without additives after formation cycling.

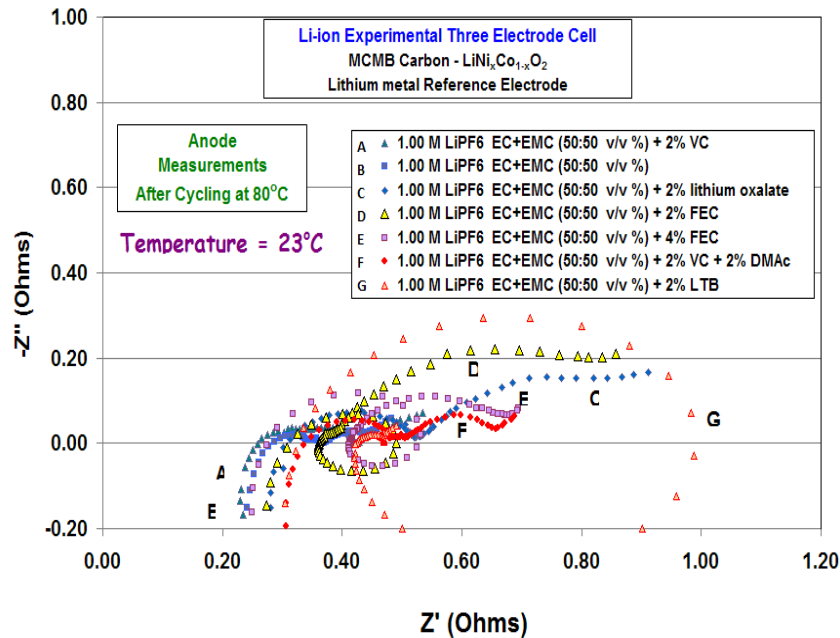


Figure 7. AC impedance (Nyquist) plots of MCMB electrodes in MCMB-LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> cells containing 1.0M LiPF<sub>6</sub> EC+EMC (50:50 v/v %) electrolyte with and without additives after being subjected to high temperature cycling.

When the electrochemical impedance behavior of the full cells was analyzed at after completing each of the 20 cycle increments at high temperatures, similar trends were displayed as observed for the  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cathodes. This finding is consistent with the fact that the overall cell impedance was observed to be dominated by the contribution of the  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cathodes.

#### Tafel Polarization Measurements of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ and MCMB Electrodes

To complement the EIS results described above, the lithiation/de-lithiation kinetics were determined for both the anode and the cathode by conducting Tafel polarization measurements of the MCMB- $\text{LiNi}_x\text{Co}_{1-y}\text{O}_2$  cells. These measurements were performed while the cells were in a full state-of-charge (SOC) ( $\text{OCV} = > 4.07\text{V}$ ) before and after each cycling period. In interpreting these Tafel plots, there are distinct charge-transfer controlled regimes, where the overpotential increases linearly with  $\log(I)$ . In addition, the effect of mass transfer appears to be relatively insignificant, such that kinetic parameters, i.e., exchange current and transfer coefficients, may be calculated from the intercept and slope of the Tafel plots, respectively. When measurements were performed on the MCMB anodes after completing the formation cycling, the cell containing the 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) + 2% FEC electrolyte displayed the highest limiting current densities, as illustrated in Fig. 8, with comparable behavior also being displayed by the cells containing lithium tetraborate and lithium oxalate.

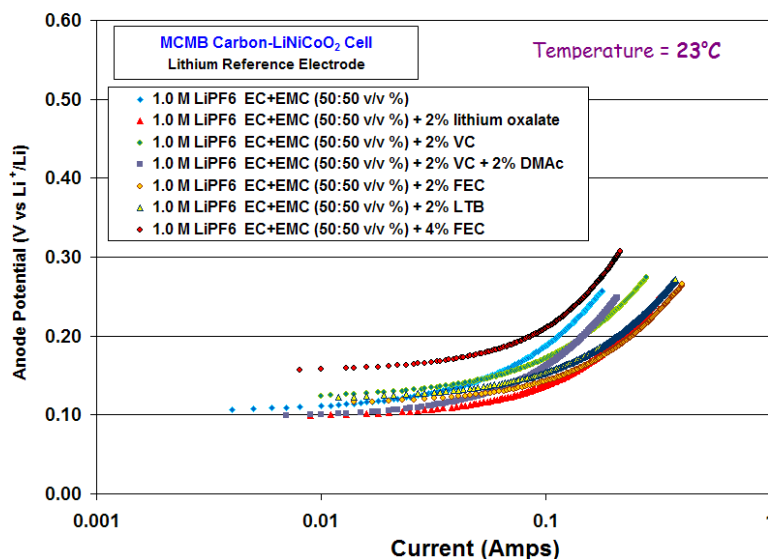


Figure 8. Tafel polarization measurements of MCMB electrodes in MCMB- $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  cells containing 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) electrolyte with and without additives after formation cycling.

When measurements were taken of the MCMB anodes after the cells had been subjected to high temperatures cycling (i.e., 20 cycles at  $60^\circ\text{C}$  and 20 cycles at  $80^\circ\text{C}$ ), as shown in Fig. 9, the kinetics of Li de-intercalation were most rapid for the baseline solution followed closely by the cells containing VC, lithium oxalate, and 4% FEC as electrolyte additives. In contrast, a couple of the formulations displayed much poorer Li de-intercalation kinetics, such as the samples containing VC +DMAC and lithium tetraborate, suggesting that some deleterious interaction is occurring at high temperatures.

It should be noted that the beneficial effect of these additives, if any, at MCMB anodes within cells that are exposed to high temperature may be more dramatic when coupled with electrolyte formulations that do not contain a high proportion of ethylene carbonate. In general, much lower limiting current densities were observed when the lithium kinetics were measured for the  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  electrodes after being subjected to high temperature cycling, as shown in Fig. 10, and being consistent with finding from the EIS data. Of the electrolytes investigated, the addition of FEC was observed to impart the most beneficial effect in terms of preserving the lithium kinetics at the cathode.

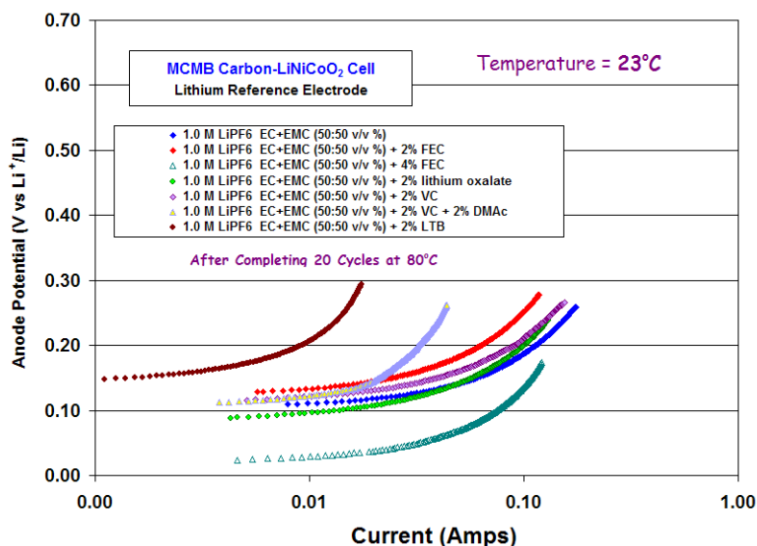


Figure 9. Tafel polarization measurements of MCMB electrodes in MCMB- $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  cells containing 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) electrolyte with and without additives after being subjected to high temperature cycling.

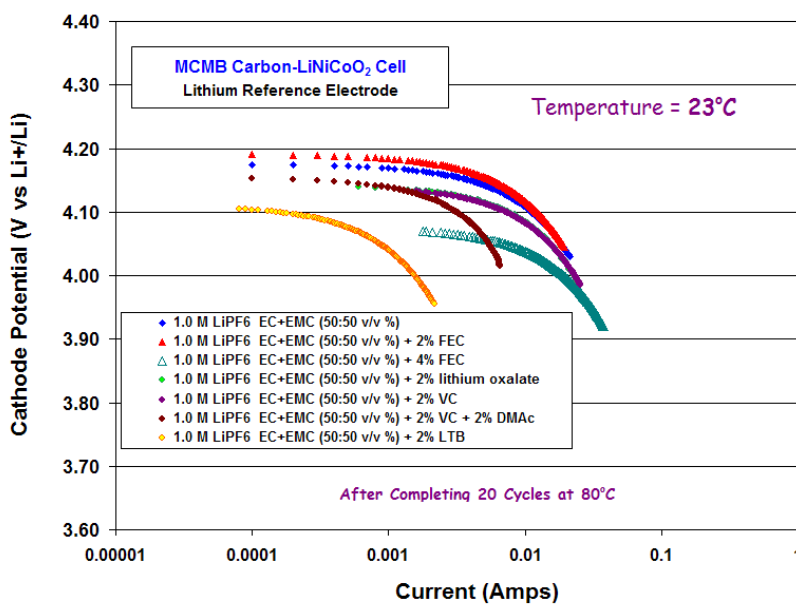


Figure 10. Tafel polarization measurements of  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  electrodes in MCMB- $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  cells in contact with 1.0M  $\text{LiPF}_6$  EC+EMC (50:50 v/v %) electrolyte with and without additives after being subjected to high temperature cycling.

## Summary and Conclusions

We have described the use of a number of electrolyte additives in experimental MCMB-  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cells, which were exposed to temperatures as high as  $80^\circ\text{C}$ . The additives investigated include, vinylene carbonate (VC), dimethyl acetamide (DMAc), mono-fluoroethylene carbonate (FEC), lithium oxalate, and lithium tetraborate. These additives have been added to an electrolyte solution anticipated to perform well at warm temperature (i.e., 1.0M  $\text{LiPF}_6$  in EC+EMC (50:50 v/v %)). With respect to the capacity retention upon being subjected to high temperature cycling, the cells containing the VC and lithium oxalate displayed the lowest capacity fade rates. The degradation of the anode kinetics was slowed most dramatically by the incorporation of VC and lithium oxalate into the electrolytes, whereas the greatest retention in the cathode kinetics was observed in the cell containing the electrolyte with FEC added. It should also be mentioned that due to the flooded cell design and lack of hermeticity of the experimental cells used in this study, the performance of these electrolytes in prototype cells will most certainly result in less dramatic capacity fade characteristics. However, we anticipate that the trend observed in terms of stability will most likely be similar.

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