

## Lithium Plating Behavior in Lithium-ion Cells

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### ABSTRACT

A Li-ion cell does not contain metallic lithium under normal conditions of operation. Under strenuous charge conditions, however, metallic lithium may deposit on the carbon anode in preference to lithium intercalation and may cause problems in terms of performance, reliability and safety of the cell. Factors that affect the anode polarization and also Li intercalation kinetics play a crucial role in determining the propensity for such lithium deposition. Such factors include the nature of electrolyte, anode/cathode capacity ration, which have been studied with specific examples here. Further, various prototype cells from different manufacturers have been examined for their susceptibility towards lithium plating from a set of systematic charge/discharge tests at different charge rates and temperatures.

### 1.0 INTRODUCTION

In a lithium-ion cell, lithium ions undergo intercalation reactions at both electrodes, shuttling from the galleries of the metal oxide positive electrodes into the galleries of the carbonaceous anodes upon charge and vice versa on discharge. Under nominal conditions of operation, there is no presence of metallic lithium in the cell. However, more strenuous conditions of charge, deposition of metallic lithium can occur on the carbon anode instead of Li intercalation into it, due to a reduction in the intercalation kinetics at the anode. Such conditions include high charge rates combined with low charge temperatures. Among various anode materials that are currently in use, graphitic anodes are more susceptible to lithium plating, due to the proximity of its reversible potential to Li, while coke, hard carbons and especially lithium titanate anode are less susceptible to lithium plating. The plated lithium is largely reversible and will oxidize at potentials about 100 mV higher than the lithium deintercalation potentials, thus resulting in a high voltage plateau preceding the usual discharge profile, as shown in Fig. 1.<sup>(1,2)</sup> The high voltage plateau in the discharge curve is thus a semi-quantitative indication for the lithium plating that would have occurred in the preceding charge.

Unfortunately, the effects of lithium plating are not as benign and do not disappear entirely during the subsequent discharge. It is possible that some of the lithium thus plated may reoxidize during the subsequent discharge or intercalate ‘chemically’ into graphite, given sufficient time. Any residual lithium that remains on the surface, however, reacts readily with the electrolyte and degrades the anode/electrolyte interface

and even forms 'passivated and isolated lithium. The loss of reversible lithium thus causes a rapid decay in the performance. More seriously, lithium plating is known to be dendritic, often inducing internal shorts, which will pose serious problems, both in terms and reliability and safety of Li-ion cells.

Apart from the operating conditions of high charge rates and low temperatures, there are several cell design aspects that will accentuate the propensity towards Li plating. Anode materials that have high reversible potentials (more positive to lithium), for example coke, will be less amenable for such lithium plating, while graphite, with its reversible potential close to, with 100 mV of, lithium deposition potential will be more susceptible. Further, the ratio of anode capacity to cathode capacity is a critical parameter. Li-ion cells generally have excess anode capacity compared to cathode, but a reduced amount of anode reserve will polarize the anode to lithium deposition potentials. The anode is required to be larger, not only in capacity, but also in area and dimensions to avoid edges that are prone to lithium plating.<sup>(3)</sup> Finally, the nature of electrolyte is a critical parameter that can affect the intercalation kinetics and thus the plating behavior. Based on several studies performed at JPL<sup>(1-4)</sup> and elsewhere<sup>(5,6)</sup>, it is evident that electrolyte plays a strong role in defining the interfacial conditions at the anode and in determining the SEI on its surface. Lithium intercalation kinetics in graphite, especially at low temperatures, can be controlled by a judicious selection of electrolyte solution, i.e., either solvent or salt.<sup>(4-6)</sup> In this paper, we illustrate the strong effect of electrolytes on the Li intercalating kinetics at the anode and thus on the plating behavior, with two specific examples, i.e., i) electrolyte solutions containing high and low proportions of ethylene carbonate, the component responsible for the SEI formation, and ii) electrolytes with and without SEI-stabilizing additive, e.g. vinylene carbonate (VC). Further various prototype cells have been examined for their vulnerability toward lithium plating, using a systematic study of their charge characteristics at different rates and at different temperatures

## EXPERIMENTAL

The effects of different electrolytes on lithium plating were determined in three-electrode, O-ring-sealed, glass cells containing spiral rolls of MCMB 1028 graphite anode and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathodes (both supplied by Yardney Technical Products), and lithium reference electrodes separated by two layers of porous polypropylene. The electrolytes contained carbonate-based solvents (EC, DMC, DEC and EMC), with  $\text{LiPF}_6$  salt in the desired concentration, and were purchased from Mitsubishi or Ferro Corporation with less than 50 ppm of water. The capacities of these cells are typically around 300-400 mAh at 25°C. DC electrochemical measurements were performed using an EG&G Potentiostat / Galvanostat interfaced with an IBM PC, using Softcorr 352. Charge - discharge measurements and cycling tests were carried out on these test cells with an Arbin battery cycler.

Prototypes cells for these studies consisted of both prismatic and cylindrical configurations, with either liquid or gel electrolytes, either in metallic containers or

plastic encasements (pouch cells) and were supplied by Yardney Technical Products, Quallion Systems, SKC and ABSL. Apart from cell design variations, there are also differences in their chemistries, i.e., nature of anode and cathode materials, composition of the electrolytes, and in some cases ratio of cathode capacity to anode capacity. Charge-discharge measurements and cycling tests were performed with a Maccor battery cycler. A Tenney environmental chamber was used to maintain the desired temperature within  $\pm 1^\circ\text{C}$  for the cells (convectively cooled). Temperature measurements were performed using thermocouples attached to the cells.

## RESULTS AND DISCUSSION

As mentioned above, the presence of metallic Li over graphite anode would manifest as a upper voltage plateau in the discharge curve in subsequent discharge, as illustrated in Fig. 1. Also, the width of the plateau is proportionate to the amount of metallic lithium, and understandably increases after successive charges at low temperatures due to increased Li plating. Using this high voltage plateau as the signature for Li plating, we have examined various experimental conditions and different cell designs to assess their plating behavior.

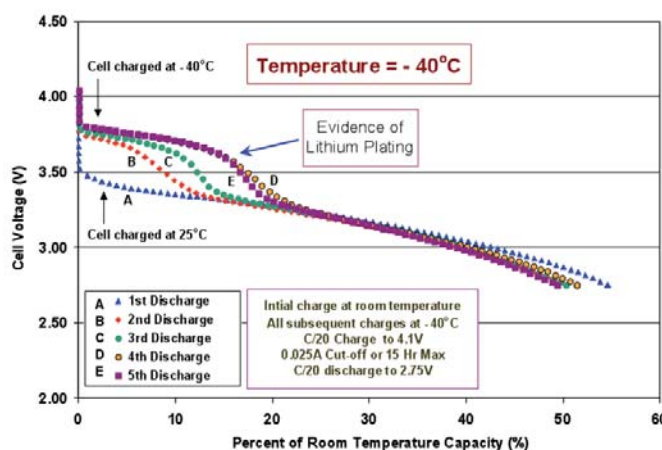


Fig. 1. Discharge curves of a Li-ion cell at C/20 at  $-40^\circ\text{C}$ , following charging both at room temperature and at  $-40^\circ\text{C}$  at a charge rate of C/20.

### 3.1 Effect of Electrolyte on Li plating

It is true that a reduction in the lithium intercalation kinetics into graphite, as may be expected at low temperatures, will drive the anode potentials to negative values (vs. Li) and lead to lithium plating on the anode surface during charging. We have shown in several of our earlier publications that the electrolyte is a strong determining factor for the lithium intercalation kinetics, especially at the anode.<sup>(3,7)</sup> A good low temperature electrolyte, as described in these reports, not only facilitates rapid ionic mobility at low temperatures, due to its low viscosity, but, more importantly, provides favorable

interfacial SEI characteristics on the anode such that the charge transfer and diffusion processes related to Li intercalation reaction are facilitated. Such an electrolyte is thus expected to minimize or eliminate the problem of lithium plating as well during low temperature charging, as demonstrated in the following examples.

### 3.1.1 Electrolyte formulations with Low EC and High EC contents

Two electrolyte formulations with 1.0 M  $\text{LiPF}_6$  dissolved in solvents with high and low EC contents, specifically i) a ternary mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) in a volume ratio of 5:3:2 (termed as High EC formulation) and ii) a quaternary mixture of EC, DMC, diethyl carbonate (DEC) in a volume proportion of 1:1:1:3 (termed as low-EC formulation) were chosen as examples here. The first electrolyte formulation provides good cyclic stability at ambient and warm temperatures and was often used by the battery manufacturers. The second formulation represents one of JPL's several electrolyte formulations for improved low temperature performance. Good low temperature performance was observed with this electrolyte down to  $-60^\circ\text{C}$  in our laboratory test cells as well as in prototype cells, and with the discharge utilization consistently superior to the high-EC formulation at all temperatures,  $\leq -20^\circ\text{C}$ .<sup>(8)</sup> These electrolytes were tested in three-electrode cells with MCMB anodes and lithiated nickel cobalt oxides cathodes, and Li reference electrodes, to understand the individual electrode polarizations and to derive basic electrochemical data on individual electrode kinetics at different temperatures.

Fig. 2A and 2B illustrate the differences between these two cells during charging, especially at low temperatures,  $-20^\circ\text{C}$ . Figure 2A shows the individual electrode potentials, cell voltage and cell current during charging at 50 mA (about C/10) at  $-20^\circ\text{C}$  for the cell containing the high EC-proportion.

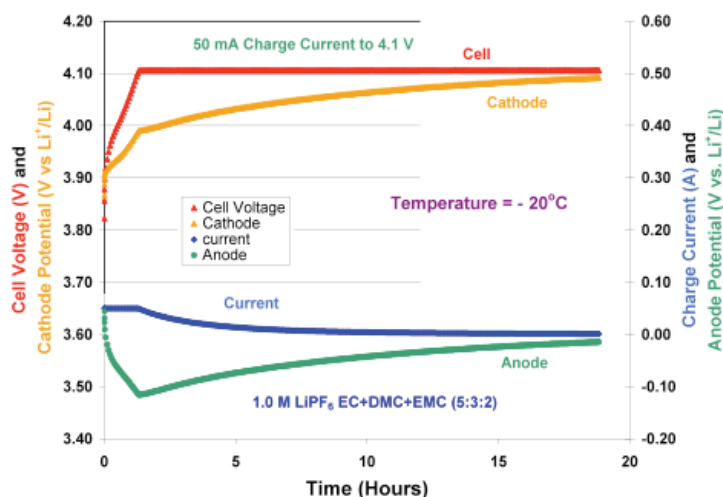


Fig. 2A: Cell potentials, Cell currents and individual cathode and anode potentials (4) in MCMB-NCO Li-ion test cells with electrolytes containing 1M  $\text{LiPF}_6$  in A) High EC, i.e., 5:3:2 EC:DMC:EMC during charging at  $-20^\circ\text{C}$  at 50 mA to 4.1 V followed by taper.

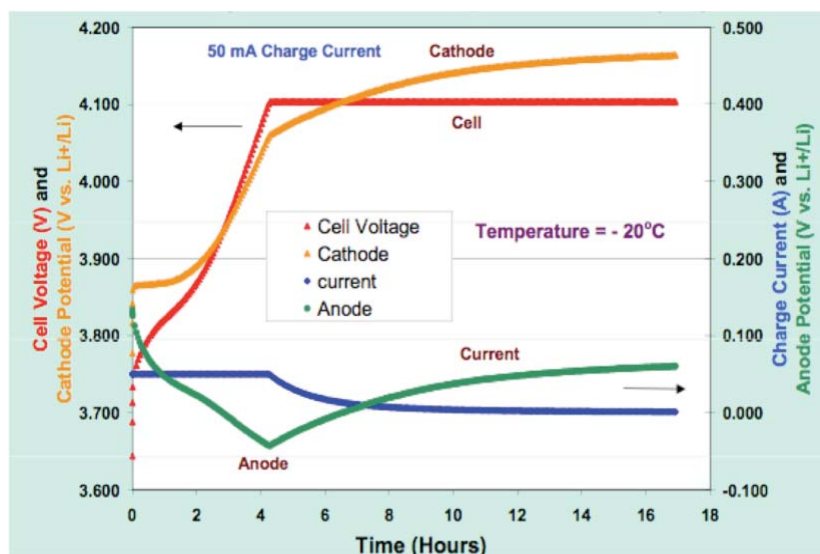


Fig. 2B: Cell potentials, Cell currents and individual cathode and anode potentials (4) in MCMB-NCO Li-ion test cells with electrolytes containing 1M LiPF<sub>6</sub> in low EC, i.e., 1:1:1:4 EC:DMC:DEC:EMC mixture during charging at -20°C at 50 mA to 4.1 V followed by taper.

The cathode potential exhibits the normal trend, i.e., to increase steeply during constant current charging, followed by a relatively slow increase in the constant voltage or tapered charge mode. The anode potential, on the other hand, has considerable undershoot, even below the lithium potential. The voltage goes as low as -120 mV vs Li and never relaxes to the positive potentials even though current continues to taper. For the entire duration of the charge, the anode potential is negative to the Li<sup>+</sup>/Li potential, which suggests a possibility for noticeable Li plating on the anode. The cell containing the electrolyte with low-EC solvent mixture (Fig. 2B), also exhibits an undershoot in the anode potential, but only for a short period at the end of the constant current charging. The anode potential becomes the most negative ( $\sim -70$  mV vs. Li<sup>+</sup>/Li) when the charge voltage and current are highest. Once the cell gets into tapered charge mode, the anode potential quickly recovers and stays in the positive territory ( $\sim 0.05$  V vs Li<sup>+</sup>/Li). Interestingly, the cathode is more polarized here by about 50 mV, suggesting that the cell polarization is distributed more uniformly here between the anode and cathode, unlike the cell with high EC-solution. Based on the sustained heavy polarization of the anode in the high-EC solution, there might be noticeable lithium plating during this charge process.

Fig. 3A and 3B display the discharge characteristics at -20°C, following the charging illustrated in Figs. 2A and 2B, respectively. There is noticeable upper voltage plateau in the discharge curve of the cell with high-EC formulation, as may be expected from the anode potentials during the preceding charge. If the charge was done at the room temperature, however, there was no plating of lithium as evident from the absence of a high voltage plateau. In contrast, the cell with low-EC content electrolyte doesn't exhibit any lithium plating (Fig. 3B), again evident from the absence of the high voltage plateau. Although the anode potential became negative in the previous charge, no lithium plating was observed with this cell in the subsequent discharge profiles. This might be

due to the fact that the potentials were not sufficiently negative and/or any lithium plated on the electrode surface could intercalate into the carbon during the taper mode.

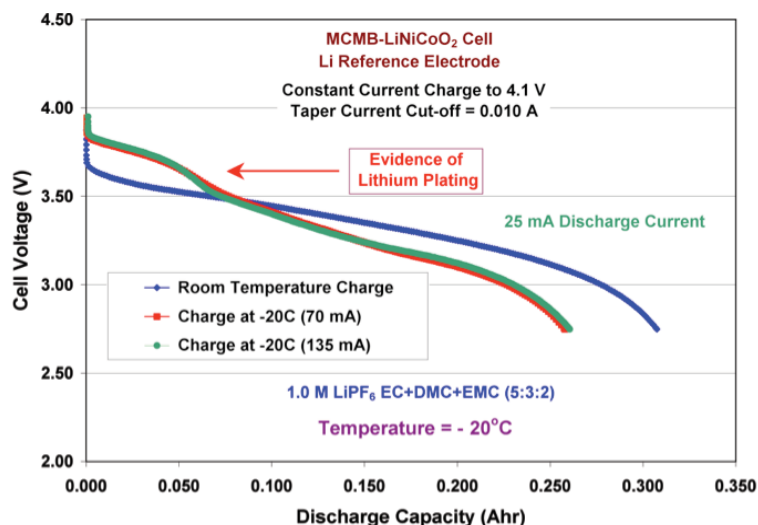


Fig. 3A: Discharge curves of MCMB-NCO Li-ion test cells with electrolytes containing 1M LiPF<sub>6</sub> in high EC, i.e., 5:3:2 EC:DMC:EMC mixture at 25 mA and -20°C, following charge at 70 mA at room temperature and -20°C.

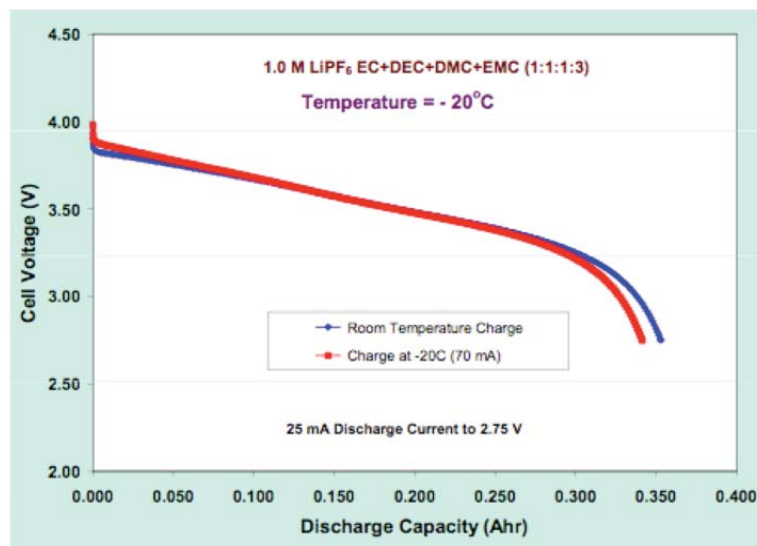


Fig. 3B Discharge curves of MCMB-NCO Li-ion test cells with electrolytes containing 1M LiPF<sub>6</sub> in low EC, i.e., 1:1:1:4 EC:DMC:DEC:EMC mixture, at 25 mA and -20°C, following charge at 70 mA at room temperature and -20°C.



### 3.1.2. Electrolyte formulations with 'filming' additives

In this example, an electrolyte additive, vinylene carbonate (VC), which has been reported to assist in the formation of robust SEI on the anode<sup>(9,10)</sup> and thus contribute to an enhanced durability at warm temperatures,<sup>(11)</sup> has been studied in electrolyte formulation containing low proportion of ethylene carbonate. The electrolyte compositions examined include i) 1.0 M LiPF<sub>6</sub> in EC+DEC+DMC+EMC (1:1:1:4 v/v %) and ii) 1.0 M LiPF<sub>6</sub> in EC+DEC+DMC+EMC (1:1:1:4 v/v %) and about 2% of VC as an additive. The low EC formulation EC:DEC:DMC:EMC::1:1:1:4 v/v % has been well demonstrated in our earlier studies to perform well at low temperatures<sup>(xx)</sup>. A combination of this solvent mixture with small additions of VC is expected to provide the synergistic effect of good low temperature performance and enhanced high temperature resilience. Once again, three electrode cells were fabricated with the above electrolyte solutions using MCMB anodes and lithiated nickel cobalt oxides cathodes and Li reference electrodes, to understand the polarization behavior and to derive basic electrochemical data on individual electrode kinetics at different temperatures.

Fig. 4 show the charge characteristics of the cells with these two electrolytes at -20°C, specifically the individual electrode potentials, cell voltage and cell current during charging at 50 mA (C/8) at -20°C for the cells with and without the VC additive. The cathode exhibits higher polarization in the electrolyte without the additive. In the electrolyte solution with the VC additive, cathode potentials are lower by more than 50 mV, especially towards the end of constant-current charge and before the onset of taper. The anode potential, on other hand, exhibits the opposite trend. The anode potential remains anodic (positive) to Li<sup>+</sup>/Li for the initial periods of charge in the electrolyte without the VC additive. With the VC additive, however, the anode potential becomes negative for a considerable duration, even after the current is tapered.

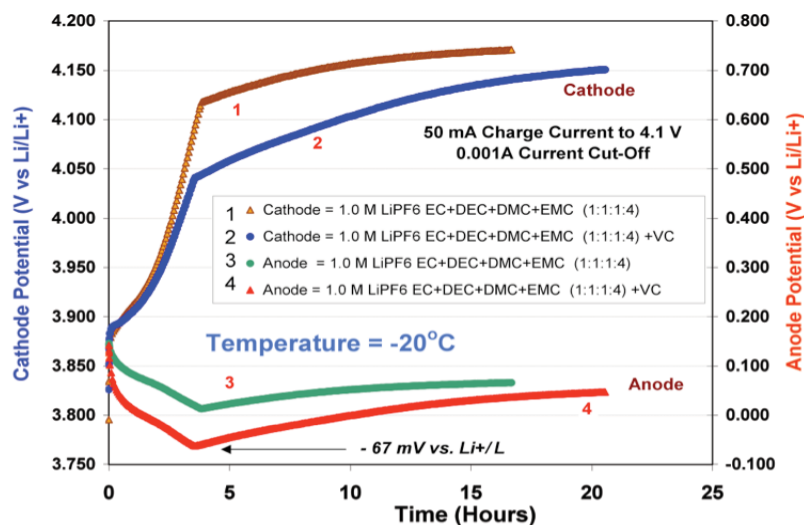


Fig.4: Cathode and anode potentials in MCMB-NCO Li-ion test cells with electrolytes containing 1M LiPF<sub>6</sub> in A) EC:DMC:DEC:EMC (1:1:1:4) without VC and B) with VC additive charging at 23°C at 25 mA to 4.1 V followed by taper.

Based on these trends, we may expect to have lithium plating in the cell containing the VC additive, which is confirmed in the subsequent discharges (Fig. 5A and 5B). There is the upper voltage plateau corresponding to lithium stripping in the cell containing the VC additive, but not evident in the cell without the additive. These disparities become more prominent at lower temperatures, at  $-30^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ , (data not shown here), with the cell without the VC additive showing no traces of Li plating, despite a little undershoot in the anode potential, while the cell with the VC additive shows pronounced high voltage plateaus characteristic of Li plating.

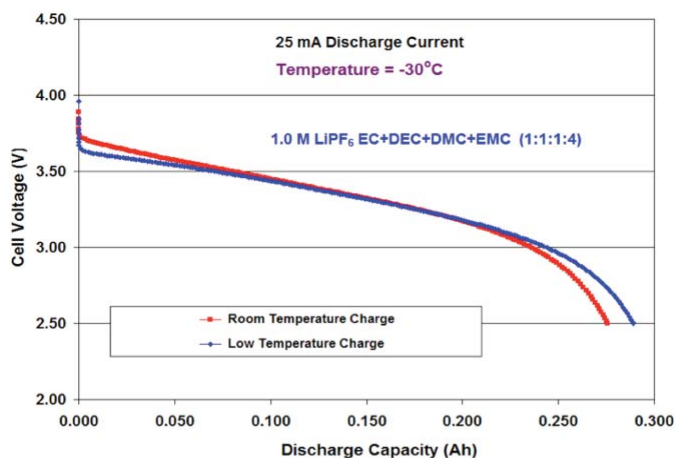


Fig. 5A: Discharge curves of MCMB-NCO Li-ion test cells with electrolytes containing 1M  $\text{LiPF}_6$  in EC:DMC:DEC:EMC (1:1:1:4) without VC additive at 25 mA and  $-20^{\circ}\text{C}$ , following charge at 70 mA at room temperature and  $-20^{\circ}\text{C}$ .

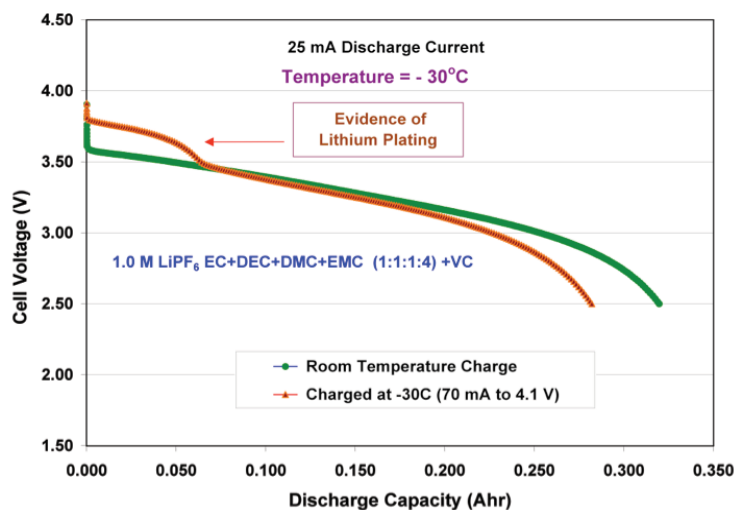


Fig. 5B: Discharge curves of MCMB-NCO Li-ion test cells with electrolytes containing 1M  $\text{LiPF}_6$  in EC:DMC:DEC:EMC (1:1:1:4) with VC additive at 25 mA and  $-20^{\circ}\text{C}$ , following charge at 70 mA at room temperature and  $-20^{\circ}\text{C}$ .



### 3.2 Li Intercalation Kinetics into anode and cathode

In order to get more quantitative understanding of the kinetics for the lithium intercalation and plating processes in EC-rich and low-EC electrolyte solutions, and with solutions containing the SEI-stabilizing additive, we performed DC polarization measurements, specifically Tafel measurements, on the individual electrodes. Such polarization curves indicate the relative kinetics of anode and cathode as shown in Fig. 6, for example, in cells with and without the VC additive. It is clear from the figure that the anode kinetics become more sluggish compared to the cathode kinetics, as the temperature is decreased, which would induce higher polarizations at the anode.

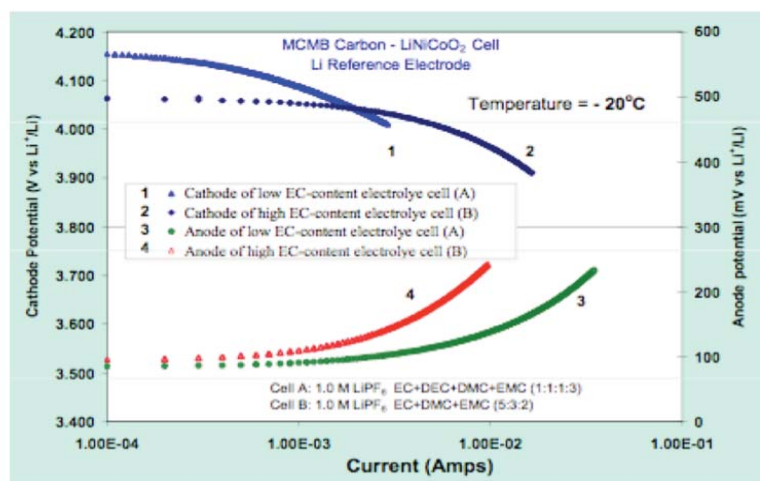


Fig. 6: Tafel curves of in MCMB anode and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode in electrolytes containing 1M  $\text{LiPF}_6$  in high EC-content and low EC-content solvent mixtures, i.e., 5:3:2 EC:DMC:EMC and 1:1:1:4 EC:DMC:DEC:EMC at various temperatures.

For a more quantitative understanding, exchange current were calculated from these Tafel data, with appropriate corrections for the mass transfer interference, and are summarized in Table -1.

Table-1: Exchange currents for Li intercalation in MCMB anode and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode in different electrolytes and at various temperatures.

Electrolyte	Electrode	Exchange Current, mA			
		25 C	0 C	"-20C	"-40C
1.0 M $\text{LiPF}_6$ EC:DEC:DMC:EMC:: 1:1:1:3	Cathode	26.00	8.20	0.40	0.20
	Anode	124.00	50.60	5.96	0.17
1.0 M $\text{LiPF}_6$ EC+DMC+EMC (5:3:2)	Cathode	24.80	16.20	3.23	0.18
	Anode	61.80	23.70	1.66	0.18
1.0 M $\text{LiPF}_6$ EC+DMC+DEC+EMC (1:1:1:4 v/v %)	Cathode	26.60	11.10	2.46	
	Anode	427.00	135.90	18.60	
1.0 M $\text{LiPF}_6$ EC+DEC+DMC+EMC (1:1:1:4) +VC	Cathode	27.30	11.84	2.35	
	Anode	152.00	41.50	4.35	

It is clear from Table-1 that the exchange currents decrease as the temperature is reduced, both for the anode and cathode reactions, in either high EC or low-EC electrolytes. Further, the anode kinetics is less favorable in the high-EC solutions at low temperature, which supports their poor low temperature performance and also their propensity towards lithium plating at low temperatures. In the low-EC formulations, on the contrary, the anode kinetics are consistently superior, which would help both in the discharge performance and in avoiding lithium plating during low temperature charging. The cathode kinetics, on the other hand, are superior in high-EC formulations, which also would favor high anode polarizations and thus Li plating. Based on the Arrhenius plot, the activation energy for the anode charge transfer process is 14.3 kCal/mol in the low-EC formulation, compared to 13.2 kCal/mol in the high-EC solution. The corresponding activation energies are 10.8 and 11.4 kCal/mol in the high-EC and low-EC solutions respectively.

The effect of vinylene carbonate additions to the electrolyte has more interesting trends. This additive was originally proposed by Saft<sup>(9)</sup> to have beneficial effect on the anode SEI.<sup>(10,11)</sup> It is assumed to undergo ‘sacrificial reduction and polymerization’ at the anode forming a robust SEI, which is expected to provide resilience to high temperature operations. Consistent with our earlier observations, the results here point to a more ‘inhibitive effect’ on the anode kinetics. Table-1 illustrates the difference in the anode kinetics with and without the VC additive in the low-E formulations. The anode kinetics are vastly inhibited upon the addition the VC additive. This is probably the effect of the VC ‘decomposition product’ over the SEI, which may provide thermal protection, but contribute to some interfacial impedance or inhibition of the kinetics. The corresponding activation energies are 10.8 kCal/mol and 12.2 kCal/mol for the cells without and with the VC additive, respectively. The cathode kinetics are quite similar in solutions with and without the additive, with the activation energies of 8.2 and 8.4 kCal/mol.

Based on the above discussions of the electrode kinetics in these solutions and their susceptibility towards lithium plating, it clear that in all cases, where there is an inhibition of the lithium intercalation kinetics at the anode, either from high proportions of EC in the electrolyte or with the ‘SEI-stabilizing’ additives, there is a greater likelihood for lithium plating.

### 3.3 Evaluation of Commercial Aerospace Cells

Various aerospace cells have been assessed for their tolerance to Li plating at high charge rates and at low temperatures. The cells included pouch cells with various (low temperature) electrolytes, and baseline 18650 cells from Quallion, prismatic cells from Yardney, Cylindrical DD cells from SAFT and pouch gel-polymer-electrolyte (GPE) cells from SKC. The cells were charged at various charge rates at different low temperatures and the upper voltage plateau in the subsequent discharges was used as the criterion to determine the propensity towards plating. Table-2 lists the behavior of various cells under such conditions. As may be seen from the above table, the propensity

for Li plating as a function of charge rate and temperature varies significantly from one manufacturer to another. These variations may be related to the difference in materials, electrode and electrolytes, and in the cell designs, more importantly the amount of anode reserve.

Table-2: Propensity of Li plating in various aerospace Li-ion cells from different manufactures under strenuous charge conditions of high charge rates am low temperatures.

Table -1: Demonstrated Li plating as a function of charge rate and temperature

Temperature	Charge rate	Yardney	A123 (COTS)	Quallion baseline (18650)	Quallion-ED1	Quallion-ED2	SKC	SAFT (EC+EMC)
	Charge Voltage	4.1 V	3.6 V	4.2	4.1	4.1	4.2	4.1
0	C/10	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C/5	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C/2	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
-10	C/10	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C/5	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C/2	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C	No Plating	Possibly	No Plating	No Plating	NA	No Plating	No Plating
-20	C/10	No Plating	No Plating	No Plating	Plating	Mild	Mild	No Plating
	C/5	No Plating	No Plating	No Plating	Plating	Plating	Mild	No Plating
	C/2	No Plating	Plating	Plating	Mild	Plating	Mild	Mild
	C	No Plating	Plating	Plating	Low capacity	Mild	Mild	Mild
-30	C/10	No Plating	Possibly	Plating	Low capacity	NA	Mild	Plating
	C/5	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
	C/2	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
	C	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
-40	C/10	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C/5	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C/2	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity

## 4.0 CONCLUSIONS

Lithium plating on the graphite anode is a parasitic process that accompanies lithium intercalation, during strenuous charge conditions, i.e., high charge rates and low charge temperatures. Such plated lithium is deleterious to the performance, reliability and safety of lithium-ion cells. Several design parameters such as the nature of electrode and electrolyte materials and the amount of anode reserve dictate the susceptibility to lithium plating. There is a strong correlation between the intercalation kinetics and the plating behavior, as demonstrated here in two different examples, i.e., solutions with high and low EC formulations and electrolytes with and with anode-filming additives. A judicious selection of electrolyte is thus one of the options to mitigate the plating and the associated failures. Finally, a systematic study was carried out to assess the plating behavior of various aerospace lithium cells of different configurations, sizes and designs.

## 5.0 ACKNOWLEDGMENTS

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