Journal of Power Sources 362 (2017) 342–348

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Additive effects in high-voltage layered-oxide cells: A statistics of mixtures approach

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HIGHLIGHTS

- Effect of electrolyte additives characterized in terms of capacity and resistance.
- Effect of additives was modeled using statistics of mixtures.
- Model indicates that performance can be optimized.

ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form
6 July 2017
Accepted 13 July 2017

Keywords:
Statistics of mixtures model
Electrolyte additives
Li-ion battery

ABSTRACT

$Li_{1.03}(Ni_{0.5}Mn_{0.3}Co_{0.2})_{0.97}O_2$ (NMC)-based coin cells containing the electrolyte additives vinylene carbonate (VC) and tris(trimethylsilyl)phosphite (TMSPi) in the range of 0–2 wt% were cycled between 3.0 and 4.4 V. The changes in capacity at rates of C/10 and C/1 and resistance at 60% state of charge were found to follow linear-with-time kinetic rate laws. Further, the C/10 capacity and resistance data were amenable to modeling by a statistics of mixtures approach. Applying physical meaning to the terms in the empirical models indicated that the interactions between the electrolyte and additives were not simple. For example, there were strong, synergistic interactions between VC and TMSPi affecting C/10 capacity loss, as expected, but there were other, more subtle interactions between the electrolyte components. The interactions between these components controlled the C/10 capacity decline and resistance increase.

1. Introduction

With the continued consumer acceptance of electrified vehicles, strategies are needed to increase the energy density of their power sources. In principle, there are many ways to do this, such as charging the cells in the power source to higher voltages, which, in turn, will increase the energy density. However, operating cells at voltages greater than about 4.1 V introduces additional aging mechanisms, such as electrolyte oxidation, which can lead to rapid performance decline.

Cell performance decline can be divided into two broad categories: capacity loss and impedance increase. One of the main causes of capacity loss is lithium trapping in the solid electrolyte interphase (SEI) layer on the graphite electrode [1–3]. Here, components of the electrolyte react to form lithiated species, thereby removing active lithium from the cell. Capacity loss at high cell voltage due to transition metal dissolution and deposition at the graphite anode has been reported in cell with cathodes of layered transition metal, Li(Ni, Mn, Co)O_2 oxides. Gilbert et al. [1] and Shkrob et al. [4] reported a correlation between Mn concentration in the graphite electrode and capacity fade. They hypothesized that the dissolution of transition metal ions was exacerbated by the side reaction process described earlier because the positive electrode was cycling at an, effectively, higher potential.

Major contributions to impedance increase have been attributed to changes at the cathode-electrolyte interface [1–3,5]. Past researchers have all used electrochemical impedance spectroscopy to probe the causes of the cell impedance increase. They found that the contributions from the oxide cathode were much greater than those from the graphite anode. Li et al. [3] performed a detailed study of the surface of $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ using X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). With cycling, there are structural changes on the particle surface. There is also evidence of shifts in the XRD pattern and indications of oxidized

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http://dx.doi.org/10.1016/j.jpowsour.2017.07.043
0378-7753/

transition metal species (e.g., Ni^{4+}) in the XAS.

Additives are an effective means to minimize capacity fade and resistance increase. Vinylene carbonate (VC) was chosen because it is known to slow capacity loss by forming a solid electrolyte interphase (SEI) layer at the anode by polymerizing [6–11]. Tris(trimethylsilyl)phosphite (TMSPi) has been reported to act at the cathode by forming a protective film [8,12–15] and is thought to mitigate corrosion reactions at the cathode. In a recent article, Peebles et al. [16] reported that the formation of a phosphorus- and oxygen-rich surface film on the oxide cathode reduced the impedance rise in high-voltage $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$/graphite coin cells. Additionally, they measured significantly lower concentrations of transition metals on the graphite anode surface when TMSPi was used as an additive. They attribute this observation to a combination of HF removal by the reaction of the trimethylsilyl groups, schematically shown in Eq. (1), and the subsequent formation of a protective cathode surface film.

$$((CH_3)_3SiO)_2P\text{-}OSi(CH_3)_3 + HF \rightarrow (CH_3)_3SiF + ((CH_3)_3SiO)_2P\text{-}OH \quad (1)$$

Indeed, Sinha et al. [17] and Dahn et al. [18] reported the synergistic effects of VC and TMSPi, where the combination of these additives improved the coulombic efficiency and decreased the parasitic side reactions in $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$/graphite cells.

The cited works probed the effects of VC and TMSPi on cell performance systematically, using one composition at a time. It can be a time-consuming process to map the entire compositional space. Combinatorial methods are often used to accelerate this screening process, helping to identify combinations of interest and, possibly, quantify the contributions of the additive to a parameter of interest. Mathematical models, built on statistics, chemical principles, or a mixture of the two, are used for this purpose [19–21].

In this work, we present the effect of two-additive electrolyte formulations (VC and TMSPi) on the performance and cycling behavior of small lithium-ion cells, charged to 4.4 V. The change in average performance data for each electrolyte composition was collected and subjected to linear regression analysis. The impact of the additives was further assessed by fitting the data from the last performance measure to polynomial equations. This general technique is used to rapidly characterize a compositional range of interest and to identify interactions between its components. Further, the model can be used to identify a potential optimum composition for a given performance metric.

2. Experimental

Materials. All electrodes studied were made by Argonne's Cell Analysis, Modeling and Prototyping facility. Details of the electrode chemistry and construction are given in Table 1. The cell chemistry and construction are given in Table 1.

A Celgard 2325 (polypropylene/polyethylene/polypropylene) separator was used. The baseline electrolyte consisted of 1.2 M $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate (EC/EMC, 3:7 w/w) (Tomiyama Chemical Industry, Japan). VC (TCI America, >97%) was distilled under a vacuum to remove trace impurities and residual water. TMSPi (Sigma Aldrich, >95%) was used as received. The electrolyte compositions are given in Table 2.

Electrochemical Cycling. All electrochemical data were collected from 2032-type coin cells using MACCOR© cyclers. Each electrolyte composition was tested in triplicate. The diameters of the positive electrode, negative electrode, and separator were 14, 15, and 16 mm, respectively. All electrodes were dried at 110 °C prior to use, and all coin cells were assembled in an argon-atmosphere at 30 °C. The electrochemical performance of these cells was characterized by a standard, previously published procedure [22].

Briefly, galvanostatic charge/discharge cycling was conducted between 3.0 and 4.4 V at 30 °C. The cycling protocol consisted of five formation cycles at a C/10 rate followed by a reference performance test (RPT). The RPT consisted of one cycle each at the C/1 and C/10 rates and a hybrid pulse power characterization (HPPC) test [1,23–25] using 2-C discharge and 1.5-C charge pulses. The first RPT will be referred to as RPT0 and serves as the basis for determining changes in cell performance. After RPT0, the cell was cycled at the C/3 rate, which included a 3-h constant voltage hold at 4.4 V. After 20 aging cycles, a RPT was performed. The cycling/RPT process was repeated until 5 RPTs and 119 C/3 cycles were accrued. Data from the five RPTs (76 cycles) were used in the calculations discussed below.

Data reduction and calculations. Values of the C/10- and C/1-rate capacity were extracted directly from the RPT data. They were normalized to the $t = 0$ value for each cell to minimize the effect of cell-to-cell variation on the capacity loss data. The average, normalized data were used for plotting.

The cell resistances were calculated from the HPPC data. The discharge resistance (R_d) was calculated as shown in Eq. (2), where t_0 is the time just before the discharge pulse, and t_1 is the time at the end of the discharge pulse.

$$R_d = \frac{V_{t_0} - V_{t_1}}{I_{t_0} - I_{t_1}} \quad (2)$$

Table 2
Electrolyte compositions studied.

Composition	Wt%		
	VC	TMSPi	Baseline electrolyte[a]
A	0.0	0.0	100.0
B	1.0	0.0	99.0
C	1.0	0.5	98.5
D	1.0	1.0	98.0
E	0.0	1.0	99.0
F	0.5	1.0	98.5
G	2.0	1.0	97.0
H	1.0	2.0	97.0

[a] 1.2 M $LiPF_6$ in EC/EMC, 3:7 w/w.

Table 1
Cell chemistry and construction.

Positive Electrode	Negative Electrode
90 wt% $Li_{1.03}(Ni_{0.5}Mn_{0.3}Co_{0.2})_{0.97}O_2$ (NMC, Toda, surface area 0.32 $m^2\ g^{-1}$)	91.8 wt% A12 graphite (Phillips 66 CPreme, surface area 2–4 $m^2\ g^{-1}$)
5 w% polyvinylidene difluoride (PVDF) binder (Solvay 5130)	6 wt% PVDF binder (Kureha 9300)
5 wt% C45 (Timcal)	2 wt% C45 (Timcal)
Active-material loading density: 9.17 mg/cm^2	Active-material loading density: 5.88 mg/cm^2
Coating thickness: 34 mm	Coating thickness: 44 mm
Al current collector: 20 mm thick	Cu current collector: 10 mm thick
Porosity: 33.5%	Porosity: 38.4%