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# Lithium ion batteries (NMC/graphite) cycling at 80 °C: Different electrolytes and related degradation mechanism

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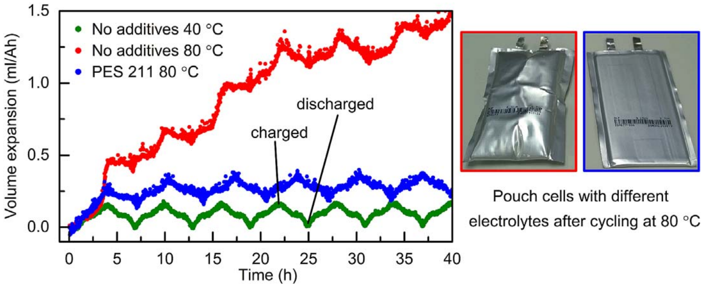
## HIGHLIGHTS

- Additives prevent initial solvent oxidation but not resistance increase of cathode.
- Surface reconstruction layer of cathode did not grow past high temperature cycling.
- New resistance layers between primary grains due to particle cracking.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

A comprehensive study on high temperature cycling (80 °C) of industrial manufactured Li-ion pouch cells (NMC-111/Graphite) filled with different electrolytes is introduced. Ageing processes such as capacity fade, resistance increase and gas generation are reduced by the choice of appropriate electrolyte formulations. However, even by using additive formulations designed for elevated temperatures a large resistance increase is observed after 200 cycles and more (which does not happen at 55 °C). Symmetrical EIS (Electrochemical Impedance Spectroscopy) shows that the cathodic charge transfer resistance is the main reason for this behaviour. Nonetheless most of the active Li is still available when cycling with suitable additives. No change of the cathode crystalline structure or a growth of the cathodic surface reconstruction layer is observed post cycling at 80 °C. Therefore a disintegration of NMC secondary particles is believed to be the main reason of the cell failure. A separation of single grains is leading to new decomposition and reconstruction layers between primary particles and an increased charge transfer resistance. Further approaches to improve the high temperature cycle stability of NMC based materials should therefore be aimed at the cathode particles morphology in combination with similar electrolyte formulations as used in this study.

## 1. Introduction

Manufacturers of Li-ion batteries specify the upper operational temperature range of their products to be approximately 50–60 °C. If operated at higher temperatures than suggested, cells have been shown to generate gas and age much faster [1–3]. However, some industrial applications require their devices to be thermally stable up to 80 °C. Such applications include cells for sensor technologies, military

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operations and downhole, high temperature environments (such as mining or oil and gas exploration) [1]. More common situations such as prolonged sunlight exposure on the dashboard of a car, can also result in temperature environments ≥75 °C [4]. Batteries containing $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC-111) as a cathode material have been reported to show an increased thermal stability compared to cells based on $LiCoO_2$ (LCO) or $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ (NCA) [5–8]. During thermal runaway tests a delayed temperature onset was observed with minor amounts of energy released. A similar observation has been reported for cells based on $LiFePO_4$ (LFP) cathodes or $Li_4Ti_5O_{12}$ (LTO) anodes [7,9,10]. However, the use of either of these materials results in lower cell voltages and worse cycling stabilities at elevated temperatures [3,11–13]. Several publications have focused on the thermal stability of Li-ion batteries at temperatures above 80 °C and higher, yet little information has been reported around investing the degradation of cells cycling under these conditions [5–7,14–17]. In a half-cell study Andersson and Edström found that the morphology and chemical composition of the solid electrolyte interface (SEI) formed on graphite anodes changed during cycling at 80 °C [18]. Lithium alkyl carbonates disappeared and LiF crystals were found to cover the surface. The degradation of the cathode material has been the focus of many studies, stating that a gain in electrode resistance of layered materials such as LCO leads to an increased capacity fade [1,19,20]. Recent publications show the importance of studying full cells for a broader understanding of degradation mechanisms, as it is believed that both electrodes can interact with each other [21–24]. Another potentially misleading observation from half-cells vs. lithium can be seen for the work published by Chang et al. [25]. An improvement in capacity retention at elevated temperatures was achieved by Ti and Fe coatings of LFP cathodes. However, when cycling the same electrodes vs. carbon anodes an adverse effect was discovered. Many other types of coatings have been applied to positive and negative electrode materials to improve the cycling stability at high temperatures [26–29]. These will not be comprehensively explored within the scope of this article. NCA, due to its high specific capacity, has been studied frequently at elevated temperatures using full cells. Sasaki and Muto et al. showed a moderate capacity retention in cylindrical cells with this cathode type at 80 °C [30,31]. After 350 cycles, approximately 80% of the capacity was still available. They found that the capacity fade directly correlated with the amount of inactive $Ni^{+2}$ and $Ni^{+3}$ areas. Both, Kojima and Muto et al. analysed NCA full cells aged at 70 and 80 °C [31,32]. They found that in addition to a phase reconstruction layer, large quantities of fluoride species were located between grain boundaries of primary particles. Recently the interest in layered $Li(Ni_{1\text{-}x\text{-}y}Mn_xCo_y)O_2$ as a positive electrode material has increased. This is linked to its advanced thermal stability compared with NCA in combination with a high specific capacity and an acceptable cycle stability [8]. These characteristics are related to large quantities of $Mn^{4+}$-ions, which stabilize the cathode structure at high state of charges (SoC) [33,34]. Bang et al. also found that the stability of these materials improves with higher Mn contents and the capacity increases with larger Ni contents within the structure [35]. This is because the redox reaction $Ni^{2+} \leftrightarrow Ni^{4+}$ primarily compensates for the charge transfer during lithiation and delithiation [34]. Bodenes et al. cycled $Li(Ni_{1\text{-}x\text{-}y}Mn_xCo_y)O_2$ vs. graphite in cylindrical cells at elevated temperatures and analysed the aged electrodes via X-ray photoelectron spectroscopy (XPS) [36,37]. In contrast to results based on NCA, they concluded that the resistance increase observed for cycling cells at 85 °C might be a result of the growing anode SEI. When cycled at 120 °C they found a migration of the PVDF binder to the cathode surface, resulting in an even faster capacity fade and resistance increase. Many of the above mentioned studies are focused on the degradation of the electrode materials. There has been minimal information given about the possible influence of electrolyte compositions used for these experiments. Most published work concerning different electrolyte formulations has been performed either on coin cell levels (half-cells vs. $Li/Li^+$) or at lower temperatures (≤60 °C). Xu et al. found that 2% of propane sultone as an additive influenced the composition of the cathode decomposition layer [38]. This resulted in a better cycle stability of coin cells following storage at 75 °C. Xia et al. used various similar substances based on sulphites, sulphates, sultones, di-sulfonates and also the well-known vinylene carbonate (VC) [39]. They cycled NMC(111)/graphite pouch cells with various mixtures of different additives at 55 °C. A combination of these substances led to improved cycling stabilities compared with single component additions. It was suggested that different additives can interact with each other but to our knowledge no mechanism was proposed which would substantiate these findings. In this study, our objective is to determine the influence of different electrolyte compositions on the cycling performance of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$/graphite pouch cells cycled at 80 °C. Additionally to study values like resistance increase, capacity fade and volume expansion also the degradation state of single cell components was evaluated. We thereby used post-mortem analyses such as symmetrical EIS measurements, surface-sensitive techniques (XPS), bulk structural measurements (XRD) and TEM/STEM.

## 2. Experimental

### 2.1. Cell filling, formation and cycling

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (NMC111)/graphite pouch cells (ca. 1.2 Ah) without electrolyte were obtained from LiFun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000, China). The electrode loading for the anode was 95 g/m² with 95% active material, 3.8% binder (CMC/SBR) and 1.2% conductive carbon. The cathode loading was 185 g/m² with 96.4% active material, 2% binder and 1.6% conductive carbon. Cells arrived vacuum sealed with extra pouch material for the degassing process still attached. Before filling with electrolyte, the cells were cut open within the excess pouch foil region and dried at 70 °C, under vacuum for at least 12 h, to remove most residual water. Afterwards each cell was filled in a dry room (dew point of -45 °C) with 4.8 g of electrolyte (4 g Ah-1). The electrolyte compositions and their suppliers can be found in Table 1.

Composition C was achieved by adding PES (Prop-1-ene-1,3-sultone – Fluorochem, 95%), DTD (1,5,2,4-Dioxa-dithiane 2,2,4,4-tetraoxide – Fluorochem, 95%) and TTSPi (Tris-trimethylsilyl-phosphite – Sigma Aldrich, 95%) to Electrolyte A. Electrolytes A, B and E exhibited a water content around 2 ppm, while the modified electrolyte C measured approximately 20 ppm (due to the water within the additives). Cells with electrolyte D were pre-filled by the manufacturer and so an analysis of the water content was not possible. After filling, the cells were transferred into a vacuum sealer (MFC-2 Solith) and underwent a soak cycle between 100 and 800 mbar before being sealed at a final pressure of 10 mbar. For the formation cycle, all cells were held for 24 h at 1.5 V in a climate chamber set at 40 °C and charged at 60 mA (C/20) to 3.8 V. A VMP3 potentiostat (Bio-Logic) was used for all electrochemical cycling. After the initial formation the cells were cut open in the dry room and resealed under vacuum (degassing step). Before cycling at elevated

**Table 1**
Electrolyte compositions for cells cycled at 80 °C – the salt concentration for each composition was 1 M $LiPF_6$ except for electrolyte E where it was 1.2 M $LiPF_6$.

| No. | Solvents (vol. Ratio) | Additives (mass ratio) | Supplier | Colour Code |
|---|---|---|---|---|
| A | EC:EMC (3:7) | none | BASF (LP57) | Orange |
| B | EC:EMC (3:7) | 1% VC | Soulbrain | Red |
| C | EC:EMC (3:7) | 2% PES, 1% DTD, 1% TTSPi | Electrolyte A modified | Green |
| D | EC:PC:DEC (35:30:45) | 1% VC, 1% PES + other | LiFun Technology | Blue |
| E | EC:EMC (1:3) | 15% FEC, 3% VC | Soulbrain | Purple |