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A detailed thermal study of a $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2/LiMn_2O_4$-based lithium ion cell by accelerating rate and differential scanning calorimetry

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HIGHLIGHTS

- Performance of a thermal study of a lithium-ion battery (NCM/LMO vs. hard carbon).
- Thermal stability primarily depends on the positive electrode–electrolyte reaction.
- Inhibition of the oxidation reaction due to oxygen release can be seen in ARC studies.
- Completion of XRD studies and identification of several reduction products.
- Impact of the SOC studied by a combination of DSC and cyclic voltammetry (CV).

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ABSTRACT

Accelerating rate calorimetry (ARC) and differential scanning calorimetry (DSC) were used to study the thermal behaviour of a commercially available lithium-ion cell. Both the complete cell (pouch type, 2 Ah) and its electrode materials, respectively, were investigated. As positive electrode material a blend system consisting of NCM ($=Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$) and LMO ($=LiMn_2O_4$) with a weight ratio of 4:1 was identified. The main exothermic behaviour is dominated by the positive electrode–electrolyte reaction. ARC studies on the positive electrode material in presence of our reference electrolyte show an inhibiting effect of the conducting salt $LiPF_6$ towards the oxidation of the organic based electrolyte by released oxygen. X-ray diffraction measurements were performed to study the thermal decomposition behaviour of the positive active material. Both the blend system and the single components, NCM and LMO, were investigated at different temperatures. A significant phase transformation from the hexagonal layered to a cubic structure as well as various reduction products could be identified. Finally, the thermal behaviour of the NCM/LMO-blend and its single phases, NCM and LMO, at different states of charge (SOC) was investigated. Therefore, detailed investigations based on differential scanning calorimetry (DSC) and cyclic voltammetry (CV) were performed.

1. Introduction

Lithium-ion cells have become promising power sources for portable applications and electric vehicles. Especially transition metal oxide based electrode materials, such as NCM (corresponding to $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$) or $LiCoO_2$ are used due to their good electrochemical performance and high capacity resulting in an acceptable high energy density [1,2]. Blend materials, commonly composed of spinel (e.g. $LiMn_2O_4$) mixed with a layered metal oxide are also commercially used [7,8]. However, concerns about the thermal behaviour of these oxide-based positive electrode materials still exist since oxygen release at higher temperatures can lead to a hazardous combustion reaction driving the flammable alkylcarbonate-based solvent of the electrolyte into fire or explosion. The thermal behaviour of complete lithium ion cells is primarily dominated by used electrode materials and their thermal decomposition behaviour as well as the reaction behaviour with the organic electrolyte [10–12]. Using C80 microcalorimetry, differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC), the thermal stability of several lithium-ion electrode materials in contact with salt-free solvent and electrolyte was already investigated by many researcher groups, e.g [3–6]. In this work, a detailed study of both the thermal behaviour of a complete

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lithium ion cell and its electrode materials was performed by accelerating rate calorimetry (ARC) and differential scanning calorimetry (DSC), respectively. The active materials for the ARC experiments were obtained from the fully charged cell after disassembling in an argon filled glove box and afterwards rinsed with dimethyl carbonate (DMC). A similar study was already performed by Maleki et al. [9]. Maleki et al. investigated complete $LiCoO_2$-based prismatic lithium ion cells (550 mAh) by ARC and the respective electrode materials in contact with electrolyte by DSC. In our case the pouch type lithium ion cell from manufacturer A (see Table 1) contained a blend composed of $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$ (NCM) and $LiMn_2O_4$ (LMO) with a weight ratio of 4:1 (w/w) as positive electrode material. So called hard carbon was used as negative electrode material. We have investigated both the complete cell and its electrode materials by ARC experiments. The work of Maleki et al. as well as recent modelling works [13] have shown that especially the reaction between the positive electrode material and the organic electrolyte dominates the thermal reaction behaviour and leads finally to a thermal runaway.

Therefore, to understand the decomposition of the NCM/LMO-blend at elevated temperatures in detail, we have carried out X-ray diffraction measurements at different temperatures. Besides the blend material, the respective single phases NCM and LMO from commercially available lithium ion cells were also investigated by XRD. Moreover, we have analysed the impact of the conducting salt $LiPF_6$ towards the reaction behaviour between the positive electrode and a $LiPF_6$ based electrolyte by ARC. DSC was used to study the influence of the state of charge (SOC) towards the thermal behaviour of the NCM/LMO-blend in contact with the electrolyte. In this case, we have also carried out DSC investigations only on the single phases NCM and LMO, respectively, to understand the influence of the state of charge more precisely.

This work aims at a detailed study of the thermal safety behaviour of a complete lithium ion cell and the correlation to its electrode materials.

2. Experimental

2.1. Investigated materials

In all thermal and electrochemical experiments, a $LiPF_6$ based electrolyte consisting of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a weight ratio of 1:1. This standard solvent mixture was commercially purchased.

Table 1 gives a short overview of the lithium ion cells and their electrode materials used for our ARC experiments. Therefore, we used three cell types from the respective manufacturer A, B, and C. In the following work, the cells will be indicated as cell A, B and C. The necessary chemical information are indicated in Table 1.

In the following, the abbreviation "NCM" always refers to the composition $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$ indicating the same ratio of nickel, cobalt and manganese. Several physical and electrochemical analyses (for instance XRD, etc.) were performed to determine and confirm the composition of the electrodes shown in Table 1.

Table 1
Overview of the lithium ion cells used for the thermal investigations.

Manufacturer [−]	A	B	C
Nominal Capacity [Ah]	2	2	1.2
Type [−]	Pouch	Pouch	Cylindric
Positive electrode [−]	NCM/LMO (4:1, w/w)	NCM[a]	LMO[b]
Negative electrode [−]	Hard Carbon	Graphite	Graphite

[a] NCM = $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$.
[b] LMO = $LiMn_2O_4$.

2.2. Thermal measurement method

2.2.1. Accelerating rate calorimetry (ARC)

To perform our ARC measurements the electrode materials were obtained from the respective commercially available lithium-ion cell from Table 1. Before disassembling, the cells had to be charged. The charge current I [A] is defined by the so called C-rate. Depending on the nominal capacity C_N [Ah] for each cell, shown in Table 1, the charge current is defined as followed (x [h^{-1}] as constant, e.g. 0.5 or 2): $I = x \cdot C_N$. Each cell was charged to 4.2 V with a defined charging rate of C/2 followed by a constant voltage step until the current dropped to a C/20 rate. Afterwards, the cell was discharged down to 2.5 V with the same current. This cycling procedure was repeated three times and ended with a final charging step up to a cut-off voltage of 4.2 V. The fully charged cell was then transferred into an argon-filled glove box and disassembled. The positive active material was scraped from the aluminium collector and rinsed with DMC to remove the original electrolyte and possible additives from the surface of the electrode material. Finally, the rinsed positive electrode material was dried under vacuum overnight to guarantee that all DMC was removed, before doing any ARC-experiments. The negative electrode material was not rinsed with DMC since organic components of the SEI could be removed by the rinsing procedure destroying the SEI [14,15].

The ARC samples, consisting of the prepared active material and the standard electrolyte (or salt-free solvent), were placed into a titanium sample holder with a wall thickness of only 0.1 mm. A sample mass of 200 mg of the cathode material and 100 mg (2:1 w/w) of the electrolyte were commonly used to carry out the ARC experiments. Due to the low density of the negative electrode material, in this case, only 100 mg of the negative electrode material and 50 mg electrolyte (2:1 w/w) were used. Since the electrode material was obtained from commercial lithium-ion cells, the weight of the electrode powder includes both conductive additives (crystalline and amorphous carbon) and binder. The whole sample preparation was made under argon atmosphere to prevent atmospheric influences (especially oxygen and water). All ARC experiments were carried out by an APTAC 254® (from Netzsch Gerätebau GmbH, Germany).

First of all, the samples were heated up to a start temperature of 80 °C. Commonly, a measurement stopped at 350 °C or when the self heating rate of the sample rised beyond 40 $°C\ min^{-1}$. In 5 K steps a heat-wait-search procedure (HWS) was applied with a waiting time of 15 min before searching for exothermal processes. If no exotherm was found, the temperature was increased with a heating rate of 5 $°C\ min^{-1}$. The threshold for an exothermic process was set to a heating rate of 0.02 $°C\ min^{-1}$. When the generated heat of our sample exceeded this threshold, the following exotherm was monitored under adiabatic conditions. Besides the detection of the temperature and the heating rate of our sample, we also recorded the pressure rise during an ARC measurement.

The ARC measurement of the complete lithium ion cell A, shown in Fig. 1, was performed at the Zentrum für Sonnenenergie- und Wasserstoff-Forschung in Ulm. The boundary conditions described above, such as heating rate or threshold for the detection of an exothermic process, were the same.

2.2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used to investigate the influence of the state of charge (SOC) on the reaction behaviour between the positive electrode material and electrolyte. The NCM/LMO-blend based lithium-ion cell from manufacturer A was therefore charged to various SOC values (namely 100%, 80%, 60%,