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Hysteresis and current dependence of the graphite anode color in a lithium-ion cell and analysis of lithium plating at the cell edge

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ABSTRACT

While charging a lithium-ion cell the color of the graphite anode changes as a function of the degree of lithiation. The color of the graphite anode is described in the literature starting from black, through red, to gold. Our ex-situ observations of the graphite anode on opened cells reveal that color differences exist at the same state of charge depending on the charge and discharge direction. This color hysteresis also remains after any length of waiting time. A current dependency of the color can also be seen, with colors which do not correspond to the average state of charge of the graphite anode. Closer investigations show that these colors are homogeneously distributed throughout the anode and do not vary with the layer depth. During charging, high states of charge and during discharging low states of charge exist on the surface of the particles compared with the average state of charge of the graphite anode. This inhomogeneity between particle surface and core subsequently equilibrates with a time constant of approx. 13 min at room temperature.

The precise color analysis of the graphite anode helps to explain another effect: the frequently occurring lithium plating on the edge of the graphite anode for cells with an anode overhang. This overhang causes overcharging of the edge area of the cathode. Lateral inhomogeneities of the lithium-ion distribution are formed in the cathode at each cycle. When charging the cell with high current, lithium plating is therefore formed first directly opposite the cathode edge. Minimizing the overhang area can substantially reduce the susceptibility to lithium plating.

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1. Introduction

Due to properties such as high capacity, high volumetric and gravimetric energy density and cycle strength, lithium-ion cells hold a key position in the field of electromobility and mobile applications. To gain a comprehensive understanding of the cell, the investigation of important processes such as intercalation and deintercalation of lithium ions in the graphite anode and hysteresis effects is crucial.

The crystal analysis of lithium-ion cells differs from in- and ex-situ investigation methods. In-situ processes such as neutron scattering and X-ray diffraction permit the investigation of the lattice spacing of the cathode and anode during the charging and discharging process, thus enabling conclusions to be drawn regarding the lithium-ion concentration [1–3].

An ex-situ process for commercial cells involves optical analysis following cell opening. Previous publications already studied the graphite color associated with different staging compounds of Li_xC_6. They reported a color gradient from black (graphite, LiC_{72}) through blue/black (LiC_{36}) and red (LiC_{12}) to gold (LiC_6) [4,5]. The observed color shift comes from absorption of photons at specific wavelengths known as drude edge [3]. In Refs. [6–10] this phenomena is also observed and used for in-situ characterization of lithium-ion batteries.

Furthermore the color allows the analysis of diffusion velocity of the deposition of lithium ions in the graphite anode [11]. Gyenes et al. showed on the basis of time-dependent color gradients the lateral redistribution to the overhang areas of the graphite anode [12]. Uhlmann et al. also describe that the occurrence of lithium plating can be seen optically as a gray deposit [9]. The damage effect of lithium plating is caused by high charge currents if the graphite potential falls below 0 V vs. Li/Li^+ [13] and leads to a loss of cell capacity by the binding of lithium ions as metallic lithium [14–16]. In the case of lithium-ion cells with anode overhang, lithium plating often begins at the cell edge [17,18].

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This paper analyzes in detail the color in the charge and discharge direction and deals with the lithium-ion redistribution after high currents. With the aid of optical analysis, the occurrence of lithium plating of lithium-ion cells in the edge area was also identified and assigned to the anode overhang.

2. Experimental

The used lithium-ion pouch cell with lithium-nickel-manganese-cobalt-oxide (NMC) cathode and a graphite anode has a capacity of 22 Ah in the voltage range of 3–4.15 V. The stacked electrodes have different geometries. The anode has an excess of 3 mm on every side. The manufacturer thus aims to prevent the cathode from projecting beyond the anode when stacked due to positioning inaccuracies, as lithium plating may then occur at this point on account of the current concentration [12].

For the further interpretation of the tests, the state of charge (SOC) refers to the anode SOC. This is differentiated from the SOC of the cell, since the anode capacity is oversized compared with the cathode capacity. An anode SOC of 50% is characterized by a voltage kink [19,20] in the cell voltage curve and can be localized at 15 Ah on the basis of Fig. 1. For our graph the cell was charged and discharged continuously with a current of C/40. The local maximum of the differential voltage dV/dQ in the charge direction helps to find the exact position of the 50% anode SOC point. 100% anode SOC is consequently achieved with an amount of charge of 30 Ah. Note that the potential curve of NMC cathode material is almost linear and is not the origin of the kink [21].

The battery test system BaSyTec XCTS is used for the investigations in this paper. The tests are conducted at a constant ambient temperature of 25° in a climate chamber. After the charge or discharge processes, the cells are opened and the colors of the graphite anode documented for optical analysis. The measurement matrix includes various charge and discharge currents between C/20 and 1C at various states of charge and various relaxation conditions through to the subsequent cell opening. The cells were opened inside an argon filled glovebox. We photographed homogeneous center regions of the graphite anode using a neutral white (3300 K) LED. Pictures were taken with a camera at about 30 cm perpendicular to the graphite surface. This allowed a very reproducible determination of the surface color. Relaxed layers (see below) did not change its color even after several days of open storage inside the glovebox. Another experimental approach is the determination of the amount of the charge capacity that can be effectively discharged (further named as "removable amount of charge") for various charging currents. The cell is charged with 3 Ah (10% SOC) using different current levels between C/20 and 2C. A subsequent discharge at a constant current (CC) of 1C is used to measure the removable amount of charge until reaching 3 V. A second experiment investigates the relaxation speed in the graphite anode. A charge current of 1C is selected, which leads to a concentration gradient of the lithium ions in the graphite anode. After different waiting times, the removable amount of charge is measured. During the experiments, we measured the cell temperature with a thermistor with resolution limit of 5 mK placed in the center of the cell.

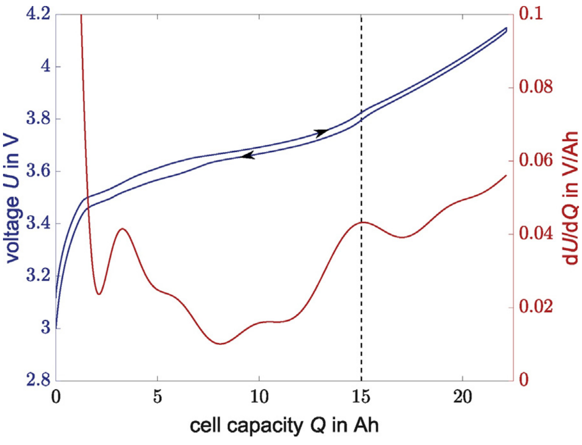

Fig. 1. Continuous voltage curve with C/40 for the cell used and its differential voltage dU/dQ. The anode potential shows a kink at $Li_{0.5}C_6$ and the differential voltage a local maximum.

Primary tests on the plating behavior of the cell in the edge area show that 4 cycles at 25° with constant charging current of 2.5 C until 4.15 V without a constant voltage (CV)-phase are already sufficient to cause lithium plating (cf. Fig. 8 a1). To analyze the effect of the increased lithium plating at the cell edge, cells with 3 V (0% cell SOC) and 4.15 V (100% cell SOC) are stored at 60° for a week and their plating behavior is compared with cells that were not subjected to heat treatment. Subsequently, the 4 charge cycles at 25° with CC of 2.5 C until 4.15 V are completed and compared with the previous results. All discharge currents for this section are CC with 1C down to 4.15 V and a CV-phase current limit of C/40.

3. Results and discussion

3.1. Color in relation to different degrees of lithiation

The color of the graphite anode results from the different lattice spacing of the graphite layers depending on the degree of lithiation. Until the fully charged state is reached, the volume of the graphite anode increases by approx. 10.4% [22,23]. Depending on the degree of lithiation, the color is produced under white light less the absorbed color components as a reflection [3].

For Fig. 2 multiple cells were charged with C/20 to the desired state of charge and then opened. This low charge current produces a homogeneous distribution of the lithium ions in the graphite anode. Fig. 2 shows a cutout with an area of approx. 9 cm^2 in each case. It was always the center of the anode from where the squares were cut out. The recorded states of charge are between 30% and 90% anode SOC equivalent to 41–123% cell SOC. To generate the two highest anode charges, the cells for this test were overcharged to 4.28 V and 4.54 V respectively. For every cutout the RGB (red, green, blue) color values (DCI-P3) are determined by the average values of all pixels. The values can be used to reproduce the colors on a computer display.

Starting from low states of charge with a black graphite anode the color is changed from black, through red, to gold with a very high state of charge. These results coincide with Refs. [7–9] and are now used to interpret the following tests.

3.2. Hysteresis in color

The familiar voltage hysteresis (Fig. 1) is expressed through a discernible difference between charging and discharging with the same SOC. So the question now arises whether the color also exhibits differences between charge and discharge direction. To this end, the states of charge 50%, 55% and 60% anode SOC are applied both in the charge direction and in the discharge direction with a current of C/20 and the cell then opened directly. The starting point for charging the cell is a voltage of 3 V and for discharging a voltage of 4.15 V. The resulting color of the graphite anode after the cell is opened is illustrated in Fig. 3. It is clearly observable that the color is different after charging or discharging with all states of charge. This can be explained by a different graphite structure at the same SOC which has been observed in Refs. [24–27], too. The reddish color of the discharge is also not

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