Journal of Power Sources 396 (2018) 444–452

Contents lists available at ScienceDirect

Journal of Power Sources

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

Temperature-dependent cycling performance and ageing mechanisms of $C_6/LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ batteries

Dongjiang Li[a,b], Hu Li[a], Dmitri Danilov[b,c], Lu Gao[c], Jiang Zhou[d], Rüdiger-A. Eichel[b,e], Yong Yang[a,**], Peter H.L. Notten[b,c,f,*]

[a] State Key Lab for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China
[b] Forschungszentrum Jülich, Fundamental Electrochemistry (IEK-9), D-52425, Jülich, Germany
[c] Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands
[d] Tianjin Lishen Battery Joint-stock Co., Ltd, Tianjin, 300384, China
[e] RWTH Aachen University, D-52074, Aachen, Germany
[f] University of Technology Sydney, Broadway, Sydney, NSW, 2007, Australia

HIGHLIGHTS

- EMF curves are regularly determined during cycling.
- Individual electrode degradation is investigated by dV_{EMF}/dQ.
- Cathode dissolution is confirmed by the XPS analysis on anode.
- CEI layer is confirmed and investigated by XPS analyses.
- Cathode degradation mechanism including dissolution and decomposition is proposed.

ARTICLE INFO

Keywords:
Layered-oxid cathode materials
Solid-Electrolyte-Interface
Cathode-Electrolyte-Interface
Capacity loss
Electromotive force
Derivative voltage analysis

ABSTRACT

Ageing mechanisms of NMC-based Li-ion ($C_6/LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) batteries have been investigated under various cycling conditions. The electromotive force (EMF) curves are regularly determined by mathematical extrapolation of voltage discharge curves. The irreversible capacity losses determined from the EMF curves have been investigated as a function of time and cycle number. Parasitic side reactions, occurring at the cathode and anode, determine the charge-discharge efficiency (CDE) and discharge-charge efficiency (DCE), respectively. The recently developed non-destructive voltage analysis method is also applied to the present battery chemistry. The decline of the second plateau of the dV_{EMF}/dQ curves upon cycling is considered to be an indicator of graphite degradation whereas the development of the third peak in these derivative curves is considered to be an indicator for electrode voltage slippage. X-ray Photoelectron Spectroscopy (XPS) measurements confirm the deposition of transition-metal elements at the graphite electrode, indicating dissolution of these metals from the cathode. Furthermore, XPS analyses confirm the existence of a Cathode-Electrolyte-Interface (CEI) layer. The outer CEI layer is composed of various compounds, such as carbonate-related Li salts, LiF and NiF_2, *etc.*, while the inner CEI layer is dominantly composed of fluoride-related compounds, such as NiF_2. Finally, a cathode degradation model including transition-metal dissolution and electrolyte decomposition is proposed.

1. Introduction

The demand for large-scale rechargeable batteries in the application of electric vehicles and smart grids has been growing rapidly in the past few years. Higher energy density combined with long cycle life and high safety is one of the key requirements in these applications. Lithium nickel-manganese-cobalt oxide (NMC) cathode material is considered to be a promising candidate for high-energy-density batteries, due to their larger theoretical specific capacity (≈260 $mAh\cdot g^{-1}$) compared to olivine ($LiFePO_4$, 160 $mAh\cdot g^{-1}$) or spinel materials ($LiMn_2O_4$, 150 $mAh\cdot g^{-1}$) [1–3].

The ternary NMC electrode system contains a large group of family

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[*] Corresponding author. Forschungszentrum Jülich, Fundamental Electrochemistry (IEK-9), D-52425, Jülich, Germany.
[**] Corresponding author. State Key Lab for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.
E-mail addresses: yyang@xmu.edu.cn (Y. Yang), p.h.l.notten@tue.nl (P.H.L. Notten).

https://doi.org/10.1016/j.jpowsour.2018.06.035
Received 18 April 2018; Received in revised form 30 May 2018; Accepted 8 June 2018

members, including $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC(111)), $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NMC(532)), $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC(622)), $LiNi_{0.425}Co_{0.15}Mn_{0.425}O_2$, $LiNi_{0.25}Co_{0.5}Mn_{0\ 25}O_2$, *etc*. These compounds commonly have a layered structure, which is similar to that of $LiCoO_2$ [4]. Electronic structure studies have shown that NMC consists of Ni^{2+}, Mn^{4+} and Co^{3+} in the as-made materials [5–8]. Ni^{2+} will be oxidized to Ni^{4+} during the initial stages of charging, while Co^{3+} will be oxidized to Co^{4+} in the higher voltage range. Mn^{4+} remains inactive throughout normal charging and provides structural stability. The NMC electrode has a similar or higher achievable specific capacity compared to $LiCoO_2$ when cycled in the potential window of 2.5–4.3 V. Advantageously, the cycling ability of the NMC electrode is better than that for $LiCoO_2$ due to its higher thermal stability [9,10].

A lot of research has been carried out to investigate the degradation mechanisms of NMC batteries [11–23]. Generally, Li immobilization in the Solid-Electrolyte-Interface (SEI) at the graphite electrode is considered to be the main origin of the battery capacity losses [24–29]. The cathode material decay becomes significant under severe aging conditions, *e.g.* at high temperature, using high (dis)charge currents and upon overcharging [30–33]. The degradation mechanism of NMC electrode is still under discussion. It is well known that the NMC material experiences a phase transition from the rhombohedral space group $R\bar{3}m$ (initial “O3” phase) to the monoclinic space group C2/m (“O1” phase) when the charge voltage is beyond 4.4 V *vs* Li^+/Li [14]. The “O1” $Li_yNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ phase has been clearly observed at $y \approx 0.3$ [34]. Cycling above this phase transition voltage (> 4.4 V) will lead to a faster capacity decay of the cathode. High currents [9] and voltages [1] are believed to be more detrimental to cause such distortion at the surface of these materials. Metal dissolution from the NMC electrode in acidic solutions ($LiPF_6$ based electrolytes) and at high temperatures has also been reported [35–40]. Metal dissolution occurs at various State-of-Charge (SoC) and is therefore considered a common degradation phenomenon.

In the present work, the aging mechanisms of NMC(111) batteries under various cycling currents and temperatures have been investigated. The irreversible capacity losses, as determined from extrapolated EMF curves, are discussed. Graphite degradation and electrode voltage slippage are unraveled by voltage derivative analyses. Cathode dissolution and subsequent metal ion deposition at the anode is confirmed by XPS analyses. Moreover, the composition of the Cathode-Electrolyte-Interface (CEI) layer formed at the cathode is investigated by XPS. Finally, the cathode degradation mechanisms are proposed.

2. Experimental

2.1. Cycling experiments

For the cycling experiments a set of cylindrical NMC (ANR18650) 2.2 A h Li-ion batteries has been investigated. The electrochemical experiments were carried out with a Maccor automatic cycling equipment. The batteries, subjected to the cycling experiments, were kept in climate chambers in order to control the temperature at 40 and 60 °C.

Before conducting the cycling experiments all batteries were activated for 5 cycles and characterization cycles were subsequently carried out at 40 and 60 °C, corresponding to the cycling temperatures, in order to derive the electromotive force (EMF) curves. During characterization all batteries were charged in the constant-current constant-voltage (CCCV) mode. A 0.5 C charging rate was used in the CC-mode followed by CV charging at 4.2 V during 1 h. The batteries were then discharged at various constant currents (0.1, 0.2, 0.3, 0.5 and 1.0 C-rates) in the subsequent cycles, using a cut-off voltage of 3.0 V. On the basis of these sets of discharge curves, the EMF was extracted by mathematical extrapolation. Details of the EMF estimation can be found in our previous publications [27,29,41–43].

After the characterization process has been completed all batteries were cycled under various conditions summarized in Table 1. The second column shows the various (dis)charging currents and the last column shows the duration of each cycle. Since the cycling time of each cycle is strongly dependent on the current, the duration of each cycle varies in different experiments. Note that the actual duration of each cycle for a given discharge current is also varying due to the decreasing battery capacity upon cycling, as is indicated by the duration range indicated in Table 1. All batteries were regularly re-characterized after approximately every 20 days.

Table 1
Cycling conditions of the NMC batteries.

	Temperature		Duration of each cycle (hours)
	40 °C	60 °C	
(dis)charging current (C-rate)	0.1	0.1	25–22
	0.3	0.3	8.2–7.1
	0.5	0.5	5.4–4.0
	1.0	1.0	3.9–3.3

2.2. XPS measurements

In order to investigate the degradation mechanisms of both the anode and cathode upon cycling, X-ray Photoelectron Spectroscopy (XPS) have been carried out on both the graphite and NMC electrodes, dismantled from the batteries after cycling under the various conditions. The batteries were fully discharged at a 0.5 C-rate before opening in an Argon glove box, and small pieces of the electrodes were cut and rinsed by pure solvent (Dimethyl Carbonate). The samples were transferred to the XPS equipment in a closed container in order to reduce the influence of moisture and air. XPS analyses were carried out on a Quantum 2000 ESCA spectrometer (Physical Electronics, USA), using an Al K_α monochromatic irradiation (1486.6 eV) at a working pressure smaller than $7 \cdot 10^{-8}$ bar. Depth profiling was carried out, using Ar ion-beam sputtering with 500 eV. The sputtering rate was equivalent to 0.26 nm/s on Ta_2O_5.

3. Results and discussion

The NMC batteries have been cycled at various currents at 40 and 60 °C. Fig. 1a shows an example of a set of characterization curves at 60 °C and corresponding extrapolated EMF curve. Fig. 1b shows an example of the development of the voltage discharge curves upon cycling at 1 C at 60 °C. Both the capacity and voltage plateaus decrease upon cycling, indicating a decline of the discharge storage capacity and voltage degradation. Fig. 1c shows the corresponding extrapolated EMF curves at the indicated cycle numbers. Similar to the discharge curves, a contraction of the EMF curves upon cycling is also observed. Obviously, the voltage plateaus in the EMF curves are more distinguishable and at higher voltage levels than in the discharging curves, due to the overpotential contribution under current flowing conditions.

The capacities extracted from both the discharge curves and EMF curves are defined as the discharge capacity (Q_d^t) and maximum storage capacity (Q_{max}^t), respectively. Fig. 1d shows the development of Q_d^t (black curve) and Q_{max}^t (red curve) at 60 °C at 1C-rate as a function of cycle number. In line with the conclusion obtained from Fig. 1b and c, Q_{max}^t is always larger than Q_d^t. The apparent capacity loss is calculated from

$$\Delta Q_{app} = Q_d^0 - Q_d^t, \tag{1}$$

and the irreversible capacity loss is calculated from

$$\Delta Q_{ir} = Q_{max}^0 - Q_{max}^t. \tag{2}$$

Obviously, the development of ΔQ_{ir} is less significant than that of ΔQ_{app}. ΔQ_{app} includes the irreversible capacity loss and the capacity loss due to the battery polarization, *i.e.* impedance increases. The