IEC TS 62607-4-5

Edition 1.0 2017-01

TECHNICAL SPECIFICATION

colour
inside

Nanomanufacturing – Key control characteristics – Part 4-5: Cathode nanomaterials for nano-enabled electrical energy storage – Electrochemical characterization, 3-electrode cell method

IEC TS 62607-4-5:2017-01(en)

THIS PUBLICATION IS COPYRIGHT PROTECTED
Copyright © 2017 IEC, Geneva, Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either IEC or IEC's member National Committee in the country of the requester. If you have any questions about IEC copyright or have an enquiry about obtaining additional rights to this publication, please contact the address below or your local IEC member National Committee for further information.

IEC Central Office
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
Fax: +41 22 919 03 00
info@iec.ch
www.iec.ch

About the IEC
The International Electrotechnical Commission (IEC) is the leading global organization that prepares and publishes International Standards for all electrical, electronic and related technologies.

About IEC publications
The technical content of IEC publications is kept under constant review by the IEC. Please make sure that you have the latest edition, a corrigenda or an amendment might have been published.

IEC Catalogue - webstore.iec.ch/catalogue
The stand-alone application for consulting the entire bibliographical information on IEC International Standards, Technical Specifications, Technical Reports and other documents. Available for PC, Mac OS, Android Tablets and iPad.

IEC publications search - www.iec.ch/searchpub
The advanced search enables to find IEC publications by a variety of criteria (reference number, text, technical committee,…). It also gives information on projects, replaced and withdrawn publications.

IEC Just Published - webstore.iec.ch/justpublished
Stay up to date on all new IEC publications. Just Published details all new publications released. Available online and also once a month by email.

Electropedia - www.electropedia.org
The world's leading online dictionary of electronic and electrical terms containing 20 000 terms and definitions in English and French, with equivalent terms in 16 additional languages. Also known as the International Electrotechnical Vocabulary (IEV) online.

IEC Glossary - std.iec.ch/glossary
65 000 electrotechnical terminology entries in English and French extracted from the Terms and Definitions clause of IEC publications issued since 2002. Some entries have been collected from earlier publications of IEC TC 37, 77, 86 and CISPR.

IEC Customer Service Centre - webstore.iec.ch/csc
If you wish to give us your feedback on this publication or need further assistance, please contact the Customer Service Centre: csc@iec.ch.

IEC TS 62607-4-5

Edition 1.0 2017-01

TECHNICAL SPECIFICATION

colour
inside

Nanomanufacturing – Key control characteristics –
Part 4-5: Cathode nanomaterials for nano-enabled electrical energy storage – Electrochemical characterization, 3-electrode cell method

INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

ICS 07.030; 07.120

ISBN 978-2-8322-3766-3

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 4-5 Cathode nanomaterials for nano-enabled electrical energy storage – Electrochemical characterization, 3-electrode cell method

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as “IEC Publication(s)”). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.

2) The formal decisions or agreements of IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested IEC National Committees.

3) IEC Publications have the form of recommendations for international use and are accepted by IEC National Committees in that sense. While all reasonable efforts are made to ensure that the technical content of IEC Publications is accurate, IEC cannot be held responsible for the way in which they are used or for any misinterpretation by any end user.

4) In order to promote international uniformity, IEC National Committees undertake to apply IEC Publications transparently to the maximum extent possible in their national and regional publications. Any divergence between any IEC Publication and the corresponding national or regional publication shall be clearly indicated in the latter.

5) IEC itself does not provide any attestation of conformity. Independent certification bodies provide conformity assessment services and, in some areas, access to IEC marks of conformity. IEC is not responsible for any services carried out by independent certification bodies.

6) All users should ensure that they have the latest edition of this publication.

7) No liability shall attach to IEC or its directors, employees, servants or agents including individual experts and members of its technical committees and IEC National Committees for any personal injury, property damage or other damage of any nature whatsoever, whether direct or indirect, or for costs (including legal fees) and expenses arising out of the publication, use of, or reliance upon, this IEC Publication or any other IEC Publications.

8) Attention is drawn to the Normative references cited in this publication. Use of the referenced publications is indispensable for the correct application of this publication.

9) Attention is drawn to the possibility that some of the elements of this IEC Publication may be the subject of patent rights. IEC shall not be held responsible for identifying any or all such patent rights.

The main task of IEC technical committees is to prepare International Standards. In exceptional circumstances, a technical committee may propose the publication of a Technical Specification when

- the required support cannot be obtained for the publication of an International Standard, despite repeated efforts, or
- the subject is still under technical development or where, for any other reason, there is the future but no immediate possibility of an agreement on an International Standard.

Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-4-5, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology standardization for electrical and electronic products and systems.

The text of this Technical Specification is based on the following documents:

Enquiry draft	Report on voting
113/317/DTS	113/342/RVC

Full information on the voting for the approval of this technical specification can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific document. At this date, the document will be

- transformed into an International Standard,
- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

A bilingual version of this publication may be issued at a later date.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

The future utilization of renewable energy technologies depends significantly on the development of efficient systems for energy storage. Conventional approaches exist for the storage of electrical energy from stationary power plants, currently fuelled by many new ideas in conjunction with the emerging "Smart Grid". For future e-mobility for individual transportation there is only one attractive solution: a battery that can store enough energy to allow all-electric driving with a range of several hundred kilometres. The current solutions already on the market can only be seen as temporary solutions. From today's perspective, lithium-ion batteries and their derivative innovative concepts are regarded as the most promising candidates. Electrodes made from nanoscale composites will play a key role in the future. Innovative materials will be developed and systematically optimized, which implies testing of a large number of different materials.

Characterization of the electrochemical properties of cathode nanomaterials used in electrical energy storage devices is important for their customized development. This document provides a standard methodology which can be used to characterize the electrochemical properties of new cathode nanomaterials that will be employed in electrical energy storage devices. Following this method will allow comparison of different types of cathode nanomaterial and comparing the results of different research groups.

This document introduces a 3-electrode cell method for the electrochemical characterization of nano-enabled cathode materials for electrical energy storage devices.

This standardized method is intended for use in comparing the characteristics of cathode nanomaterials in the development stage, not for evaluating the electrode in end-products.

The method is applicable to materials exhibiting function or performance only possible with nanotechnology, intentionally added to the active materials to measurably and significantly change the capacity of electrical energy storage devices.

In this context it is important to note that the percentage content of nanomaterial of the device in question has no direct relation to the applicability of this document, because minute quantities of nanomaterial are frequently sufficient to improve the performance significantly.

The fraction of nanomaterials in electrodes, electrode coatings, separators or electrolyte is not of relevance for using this method.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 4-5 Cathode nanomaterials for nano-enabled electrical energy storage – Electrochemical characterization, 3-electrode cell method

1 Scope

This part of IEC 62607 provides a standardized method for the determination of electrochemical properties of cathode nanomaterials such as lithium iron phosphate (LFP) for electrical energy storage devices. This method will enable the industry to:

a) decide whether or not a cathode nanomaterial is usable, and
b) select a cathode nanomaterial suitable for their application.

This document includes:

- recommendations for sample preparation,
- outlines of the experimental procedures used to measure cathode nanomaterial properties,
- methods of interpretation of results and discussion of data analysis, and
- case studies.

NOTE The very purpose of this method is to arrive at a detailed characterization of the electrodes so that individual contribution of the anode and cathode for performance and degradation could be predicted. The method can be applied for characterization of the electrode working as cathode or/and as anode.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-1, *Nanotechnologies – Vocabulary – Part 1: Core terms*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1.1
cathode nanomaterial
material used as a cathode in a nano-enabled energy storage device which contains a fraction of nanomaterial and exhibits function or performance made possible only with the application of nanotechnology

Note 1 to entry: The cathode is a multilayered foil consisting of (1) an aluminium current collector, (2) an optional adhesion promoting carbon layer (to enhance cathode layer adhesion if necessary) and (3) the cathode layer. This cathode layer consists of the active phase (e.g. lithium containing mixed oxides or phosphate, such as LFP), a conducting phase (carbon black) and an organic binder (PVDF).

3.1.2
anode material

material used as counter electrode (CE) for the electrochemical characterization of cathodes in the 3-electrode cell

Note 1 to entry: The anode may be a tape-cast graphite electrode consisting of (1) a copper current collector foil and (2) the active layer composed of graphite, a conducting phase (carbon black) and organic binder (PVDF, CMC). Alternatively, metallic lithium may be utilized as CE. Using lithium, the necessity of balancing the capacities of cathode and anode is dropped. However, the cycling stability of lithium is strongly limited in comparison to a graphite anode. Thus the choice of the counter electrode has to be adapted to the purpose of the investigation.

3.1.3
reference electrode
RE

electrode not actively involved in the battery cell reactions (charging, discharging)

Note 1 to entry: The reference electrode is placed in the cell arrangement to enable the measurement of the electrode potentials of cathode and anode. Both values are determined with respect to the RE's potential. To ensure a proper measurement, the reference electrode's potential has to be held constant. Thus a currentless contacting of this electrode is realized to prevent the formation of overpotentials. In lithium ion battery research the most common reference electrode material is metallic lithium in contact with a lithium ion containing electrolyte.

3.1.4
3-electrode screw cell

cell providing the geometrical conditions in the three electrode arrangement

Note 1 to entry: The independent electrochemical investigation of cathode and anode material is carried out in 3-electrode screw cells. This notion describes a cell in three electrode arrangement providing battery-like geometrical conditions of cathode and anode. Additionally, a lithium reference electrode is included to enable the determination of the individual electrode potentials rather than of the overall cell voltage. The cell setup includes springs and metallic current collectors and the electrode package with anode/separators + electrolyte/cathode. The reference electrode is placed between anode and cathode, separated from these electrodes by layers of separator. For this purpose, various cell designs are possible. The case study in Annex A shows a cell design based on a half-inch PFA Swagelok fitting.[1]

3.1.5
cell voltage

U_{cell}

difference of the electrochemical potentials of the cathode and the anode

3.1.6
electrode potential

difference between the electrochemical potential of an electrode in the 3-electrode cell and the potential of the RE

Note 1 to entry: Electrode potentials φ_{WE} and φ_{CE} are the differences between the electrochemical potential of the respective electrode in the 3-electrode cell and the potential of the RE. In case of intercalation electrode materials, it is determined by the lithiation state of the material. Additionally, the overpotential of the respective electrode reaction influences its potential. Consequently it is a valuable physical parameter to be determined, as it includes a significant amount of information on the individual electrodes and their actual state.

3.1.7
cell resistance

R_{el}

ohmic internal resistance of the testing cell

---

[1] PFA Swagelok fitting is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of this product.

Note 1 to entry: R_{el} is the sum of the ohmic resistivities (e.g. electrolyte, contact resistance) within the cell.

3.1.8
charge-discharge cycle

procedure which includes charging and discharging of the testing cell

Note 1 to entry: The freshly assembled cell is completely discharged. During charging, the lithium anode is biased negatively above the zero current potential, lithium cations are reduced and metallic lithium is deposited at the surface of the lithium anode. During galvanic discharge through an external circuit (load) metallic lithium is in turn oxidized at the anode, which shows a negative potential while the cathode potential is positive. Now metallic lithium oxidizes to lithium ions and dissolves in the electrolyte. Lithium ions incorporate into the crystal lattice of the cathode material. The charging/discharging processes are reversible within certain limits.

3.2 Abbreviated terms

LFP	lithium iron phosphate, $LiFePO_4$
C	graphite (layered modification of carbon)
Li	lithium
WE	working electrode, as cathode
CE	counter electrode, as anode
RE	reference electrode
PVDF	polyvinylidene fluoride
EC	ethylene carbonate
DEC	diethyl carbonate
$LiPF_6$	lithiumhexafluorophosphate (common conductive salt of lithium ion battery electrolytes)
PE	polyethylene
PFA	perfluoroalkoxy rubber
PEEK	polyether ether ketone rubber
OCV	open circuit voltage
OCP	open circuit potential
EIS	electrochemical impedance spectroscopy.

4 Sample preparation methods

4.1 General

For the electrochemical characterization of the cathode nanomaterial 3-electrode screw cells are used. The main aspects for preparation of these measuring cells are:

a) pre-treatment of the electrodes;

b) choice of the separator and selecting a proper electrolyte/ electrolyte volume;

c) applying a defined and valid pressure on the electrode/separator package;

d) mounting of reference electrode.

4.2 Reagents

4.2.1 Cathode foil

The cathode foil can be stored in a desiccator under low atmospheric moisture for the range of several days up to weeks. Previous to the assembly of the cell, cathode material is dried (see 4.3) and put into an argon filled glove box immediately after preparation to avoid contact with atmospheric moisture.

4.2.2 Anode foil

Graphite anodes are handled like the cathode foil in 4.2.1. If metallic lithium is used as anode material, the lithium foil (d = 0,25 mm) is unpacked in an argon-filled glove box and then used as delivered.

4.2.3 Reference electrode

Metallic lithium is used as RE. It is unpacked in an argon-filled glove box and then used as delivered. The raw material used in the case study was a foil of 0,25 mm thickness. To apply it as reference electrode, its thickness has to be set to approximately 0,1 mm to avoid a mechanical stressing of the WE and CE by the reference electrode. For this purpose a strip of the lithium is wrapped in polypropylene foil and manually rolled or pressed to the thickness mentioned above.

4.2.4 Electrolyte and separator

The material testing should be carried out in an electrolyte whose composition is comparable to electrolytes used in commercial batteries. Actually, these are commonly organic carbonate based solutions containing $LiPF_6$ as conductive salt. For the investigation commercial electrolyte, 1M $LiPF_6$ in 1:1 EC:DEC, with a defined purity and water content less than 5 µg/g is used. A glass fibre nonwoven fabric of about 0,2 mm thickness is used as separator material. It is dried before use in a vacuum oven (T = 80 °C, p = 1 mbar to 5 mbar, t = 12 h).

4.3 Pre-treatment of the electrode materials

Both electrode foils are dried in a compartment dryer to achieve water contents less than 100 µg/g in the active material. Exemplary drying conditions are: T = 80 °C, p = 1 mbar to 5 mbar, t = 12 h.

It is suggested to control the water content of the cathode by drying to the constant mass. The drying procedure should be proven to achieve water content of less than 100 µg/g by Karl-Fischer titration for first five cathode samples. After that the drying to the constant mass can be applied as a standard.

The electrodes examined in the 3-electrode screw cell are either punched out or laser cut from the foil material. The mass of the electrodes, $m_{\text{electrode}}$, is determined gravimetrically with an analytical balance (resolution m = 0,000 1 g). The mass of the active phase, m_{active}, is calculated by subtracting the mass of the current collector foil, $m_{\text{substrate}}$, and multiplying by the mass fraction x of the active material in the coating.

$$m_{\text{active}} = x \cdot (m_{\text{electrode}} - m_{\text{substrate}})$$

Subsequently the theoretical capacity is calculated as follows:

$n_{\text{Li}} = m_{\text{active}}/M_{\text{active}}$ [mmol]

$Q = n_{\text{Li}} \cdot F \cdot z/3\,600$ [mAh] (z = 1, F = 96 485 C/mol)

Gravimetric capacity of the electrode: $q_{\text{M}} = Q/m_{\text{electrode}}$ [mAh/g]

Gravimetric capacity of the active material: $q_{\text{A}} = Q/m_{\text{active}}$ [mAh/g]

Specific capacity of the electrode: $q_{\text{F}} = Q/A$ [mAh/cm^2]

For these calculations, the following material data shall be given:

a) mass of the electrode (mass of coated foil), $m_{\text{Electrode}}$;

b) mass of the substrate (mass of uncoated foil), $m_{\text{Substrate}}$;

c) stochiometry/molar mass of the active material, M (can be proven by chemical analysis, i.e. ICP-MS analysis);

d) mass fraction of the active material in the electrode, x;

e) electrode area, A.

4.4 Preparation of the screw cell

The cell components (Figure A.1) are cleaned with ethanol and water in an ultrasonic bath and afterwards dried in a compartment dryer. The components are stored in the compartment dryer at 70 °C to 80 °C for at least 30 min. During such heat treatment of cell components the occasionally adsorbed water from surface of components will be removed.

The warmed up components of the cell (Figure A.2) are mounted as shown in Annex A, step 1 (Figure A.3). Afterwards they are put into the glove box to assemble the electrode setup under argon atmosphere. All materials under this section shall be handled under argon atmosphere in a glove box. In the glove box the maximum O_2 content is 50 µg/g and the maximum H_2O content is 10 µg/g.

Firstly, the cathode is placed inside the cell body onto an aluminium spacer acting as current collector. The cathode is impregnated with the electrolyte (five drops, 60 mg to 70 mg , for an electrode of 1,27 cm^2 and cathode thickness of 50 µm) (see Figure A.3).

The separator with thickness of 150 µm is punched out and one layer is placed onto the cathode. It is soaked with the electrolyte (three drops, about 30 mg).

The lithium RE is prepared by cutting a thin strip of lithium (10 mm to 12 mm in length, about 0,5 mm in width) of the coil material. This thickness of the RE is set to about 100 µm by compressing the 250 µm coil material with a hand press. This metal strip is inserted into the cell through the opening perpendicular to the cell axis and placed upon the separator sandwich.

A second separator is laid on the cathode/separator/RE sandwich and wetted with three drops of the electrolyte (about 30 mg).

The graphite anode is impregnated with the electrolyte (five drops, 60 mg to 70 mg) (for an electrode of 1,27 cm^2 and anode thickness of 50 µm). Subsequently, the wetted anode is placed in the cell, on the top of the working electrode – separator setup. It is contacted from the backside with a stainless steel spacer, a spring (k = 2,87 N/mm) and the current collector stamp. Afterwards the cell main axis containing the battery components is fixed by loosely closing the screw caps.

The ring-shaped PEEK spacer is inserted in the RE opening which is perpendicular to the cell main axis. The RE strip is threaded through the spacer void, then the RE is contacted at the backside of the PEEK ring with a stainless steel spacer. The RE way is equipped with a spring (k = 2,87 N/mm) and screwed manually.

Finally, the screw caps of the anode and cathode ways are tightened up under manual pressure and a brief function test is performed by determining the potential differences between between cathode and RE and between anode and RE with a multimeter.

If the assembly was successful, stable voltages between electrodes are observed depending on the used electrode materials.

EXAMPLE For the combination of LFP for the cathode, graphite for anode, and lithium metal for the reference electrode, the following conditions are fulfilled:

Voltage of WE vs. CE: $\varphi_{WE} - \varphi_{CE} \approx$ 0,05 V to 0,5 V.

Voltage of WE vs. RE: $\varphi_{WE} \approx$ 2,8 V to 3,1 V.

Voltage of CE vs. RE: $\varphi_{CE} \approx$ 2,7 V to 3,2 V.

If any of the measured potential differences is exactly 0 V, a short circuit between the respective electrodes occurred. In this case the cell is defective and shall be completely disassembled and built up with new electrodes.

4.5 Disassembly of the screw cell

The disassembly of the cell shall be carried out under argon atmosphere to avoid any contact with toxic decomposition products, e.g. hydrofluoric acid.

The used cell components shall be stored and disposed considering maintenance of industrial health and safety standards.

5 Measurement of electrochemical properties

5.1 General

The cell is connected as follows for the measurement of charge-discharge characteristics: the working electrode (WE) of potentiostat/galvanostat is connected to the cathode and the anode is piggyback connected to the counter electrode. The reference electrode (RE) is connected to the RE connection of the potentiostat. During the charging of the cathode, the positive bias potential (pole) is applied to the cathode and the negative bias potential (pole) to the anode.

5.2 Open circuit potential

5.2.1 Demarcation of method

The open circuit potential of an electrode is its potential, measured versus the RE in currentless state. The difference of the OCPs of cathode and anode is equal to the open cell voltage which corresponds to potential difference measured directly between anode and cathode. To obtain reliable OCP and OCV values, the measurement shall be conducted after cell conditioning (5.3.2).

5.2.2 Experimental procedures and measurement conditions

The cell is connected to a potentiostat electrically. The measurement of OCP and OCV should be carried out sequentially.

To measure the OCV, the connections of the reference electrode (RE) and the counter electrode (CE) are short circuited and set onto the anode, whereas the connection to the working electrode (WE) is plugged in the aluminium stamp contacting the cathode.

The OCP measurement is carried out in three-electrode setup. In case that the potentiostat enables the simultaneous detection of WE and CE potential, the connections are: cathode – WE, anode – CE, reference electrode – RE. The duration of the measurement of OCP and OCV can vary between five minutes (test of functionality) up to two hours (data collection for analytical evaluation).

After cell formation, the electrode potentials are usually in the ranges depending on the used electrode materials.

EXAMPLE For the combination of LFP for the cathode, graphite for anode, and lithium metal for the reference electrode, the following values are observed (see Figure A.4):

OCP of WE vs. RE: $U_{\mathrm{OCP,WE}} = \varphi_{\mathrm{cathode}} \approx 3{,}0$ V to 3,8 V.

OCP of CE vs. RE: $U_{\mathrm{OCP,CE}} = \varphi_{\mathrm{anode}} \approx 0$ V to 1 V.

OCV of the cell: $U_{\mathrm{OCV}} \approx 2{,}5$ V to 3,8 V.

5.3 Potentiostatic electrochemical impedance spectroscopy (EIS)

5.3.1 Demarcation of method

Electrochemical impedance spectroscopy bases on the measurement of the complex impedance of the cell. A periodically oscillating voltage is used as excitation signal in case of potentiostatic EIS. The method allows the resolution of the polarization losses at the electrodes and ohmic losses due to electrolyte resistance and contacting.

5.3.2 Experimental procedures and measurement conditions

The cell is connected to a potentiostat with frequency response analyser by banana jacks. In dependency on the configuration of the connections, either individual electrodes or the full cell are characterized. The possible configurations are listed below:

- EIS of full cell (anode/separator/cathode): cathode = WE, anode = CE+RE, RE = empty
- EIS of the cathode: cathode = WE, anode = CE, RE = RE
- EIS of the anode: cathode = CE, anode = WE, RE = RE

The EIS measurement is performed under the conditions given below:

OCP of WE vs. RE: $U_{\mathrm{DC}} = U_{\mathrm{OCP,WE}}$

Amplitude of the alternative perturbation: $\delta_{\mathrm{AC}} = 10$ mV

Frequency of the alternative perturbation: $f = 100\,000$ Hz to 0,01 Hz

The resulting impedance spectra (see Figure A.5) describe either the full cell setup or the impedance behaviour of a chosen electrode. In the full cell spectrum the real part of impedance at the highest frequency Z_{real}(100 kHz) corresponds to the internal ohmic cell resistance R_{el}. If $R_{\mathrm{el}} > 20\ \Omega\mathrm{cm}^2$, the cell should be discarded for further experiments.

The mid- and low-frequency range of the spectra offers additional information about, for example, polarization resistances of the electrodes and transport processes.

5.4 Charge-discharge experiment (Constant Current Constant Voltage, CCCV/CC)

5.4.1 Demarcation of method

The Constant Current Constant Voltage method is a commonly used method of battery charge-discharge. Firstly, the cell is charged under galvanostatic control (CC) until an upper potential limit φ_{limit} is reached. Subsequently the potential is held for a certain time (CV) to compensate for the influence of overvoltages during CC charging. Thus a constant lithiation state of the electrodes at the end of the charging is guaranteed, independent of the current applied during the CC step.

The discharge of the cell is carried out under galvanostatic control (CC) again.

Out of the data obtained during CCCV/CC experiments (see Figure A.6), various cell properties can be calculated, for instance the capacity of the cell and the coulomb efficiency. Additionally, the internal resistance can be estimated from the IR-drop, δ_{IR},, which occurs when the cell is switched from under load to currentless state and vice versa.

5.4.2 Experimental procedures and measurement conditions

The cell is connected to a potentiostat in the following configuration:

cathode = WE, anode = CE, reference electrode = RE

Before the CCCV-measurement start, the cell shall be (electrochemically) conditioned to ensure reliable data from the experiments following afterwards. Conditioning includes the equilibration of the cell and electrochemical formation. The validity and reproducibility of the data obtained in Clause 6 under the applied conditioning procedure and parameters should be confirmed prior to the measurement for specific combination of electrode materials.

EXAMPLE For the combination of LFP for the cathode, graphite for anode, and lithium metal for the reference electrode, the following conditioning procedure and parameters can be used:

1) Equilibration: 12 hours of storage at room temperature, without electric load
2) Formation: five galvanostatic charge-discharge cycles under small load (usually 0,1 I_tAh of the theoretical capacity)

I_{charge} = 0,1 I_tA (0,1 I_tAh corresponds to Q/10 I_tAh)

$\varphi_{\mathrm{WE,\ upper\ limit}}$ = 3,8 V

$\varphi_{\mathrm{WE,\ lower\ limit}}$ = 2,5 V

The potential and current limits of the following CCCV procedure for the cathodes are:

I_{charge} = 0,2 I_tA (0,2 I_tAh corresponds to Q/5 Ah)

$\varphi_{\mathrm{WE,\ upper\ limit}}$ = 3,8 V

t_{potstat} = 7 200 s (2 h)

I_{limit} = 0,01 I_tA (10 % of I_{charge})

$I_{\mathrm{discharge}}$ = −0,2 I_tA

$\varphi_{\mathrm{WE,\ lower\ limit}}$ = 2,5 V

50 cycles

6 Data analysis / interpretation of results (see Figure A.7)

6.1 Open circuit potential

a) Calculation: none
b) Chart: cell voltage U_{cell} (= U_{OCV}) and electrode potentials $\varphi_{\mathrm{cathode}}$ and φ_{anode} (= $U_{\mathrm{OCP,WE}}$, $U_{\mathrm{OCP,CE}}$) vs. time
c) Target value: electrode potentials of cathode and anode

6.2 Electrochemical impedance spectroscopy

a) Calculation: $Z_{\mathrm{real}}/Z_{\mathrm{imag}}$ normalized: $Z{\cdot}A = Z_{\mathrm{norm}}$ [Ωcm²]
b) Chart: Nyquist-Plot: $-Z_{\mathrm{imag,\ WE}}$ vs. $Z_{\mathrm{real,\ WE}}$
   Nyquist-Plot: $-Z_{\mathrm{imag,\ CE}}$ vs. $Z_{\mathrm{real,\ CE}}$
c) Target value: internal resistance $R_{\mathrm{el}} = Z_{\mathrm{real}}$(100 kHz)

6.3 Constant current constant voltage (CC CV) charging-discharging

a) Calculation: I normalized: $i = I/A$ [mA/cm²]

specific capacity of cell during charging: $q_{\mathrm{ch}} = \int i_{\mathrm{charge}}\mathrm{d}t$ [mAh/cm²]

specific capacity of cell during discharging: $q_{\mathrm{dis}} = \int i_{\mathrm{discharge}}\mathrm{d}t$ [mAh/cm²]

= ability of the active material to store energy

gravimetric capacity q_A: $q_A = q_{\mathrm{dis}}{\cdot}A/\ m_{\mathrm{active}}$ [mAh/g]

coulomb efficiency: $\eta_{\mathrm{CE}} = q_{\mathrm{dis}}/q_{\mathrm{ch}} \cdot 100$ [%]

IR-drop: $\delta_{\mathrm{IR}} = U_{\mathrm{OCVend},i=x} - U_{\mathrm{OCVinitial},i=0}$

b) Chart: CC-CV-diagram: U, φ_{cathode} and φ_{anode} vs. t and i vs. t

capacity development: q_{A} vs. cycle number

q_{dis} vs. cycle number

η_{CE} vs. cycle number

δ_{IR} vs. cycle number

Target value: specific and gravimetric capacities q_{dis} and q_{A}

coulomb efficiency

IR-drop δ_{IR}

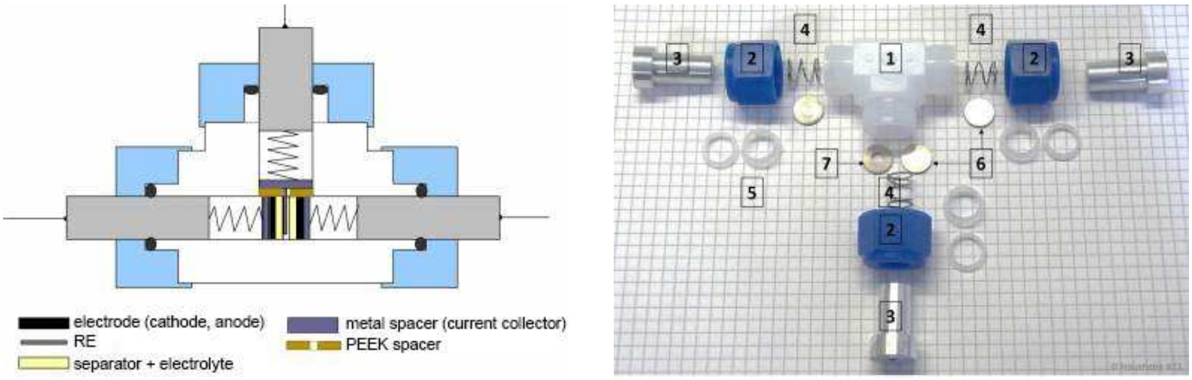
Annex A
(informative)

Case study

A.1 Sample preparation

Components which are required (see Figure A.1):

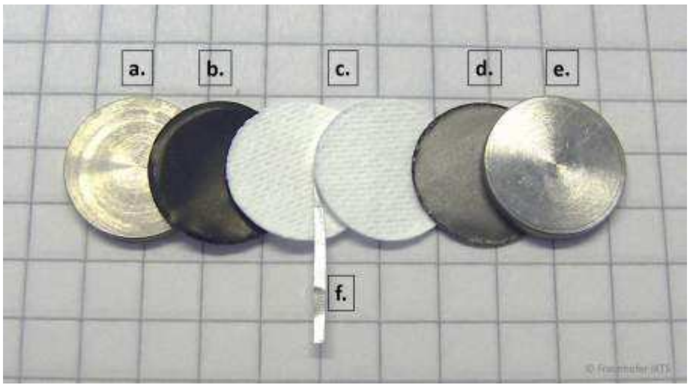
1) 1 cell body
2) 3 screw caps
3) 3 aluminium stamps
4) 3 springs
5) 3 low gaskets + 3 high gaskets
6) metal spacer (2 stainless steel, 1 aluminium)
7) PEEK spacer



IEC IEC

Figure A.1 – 3-electrode screw cell

The electrode package is structured as shown in Figure A.2, and placed between the metal spacer in the main axis of the 3-way cell body.



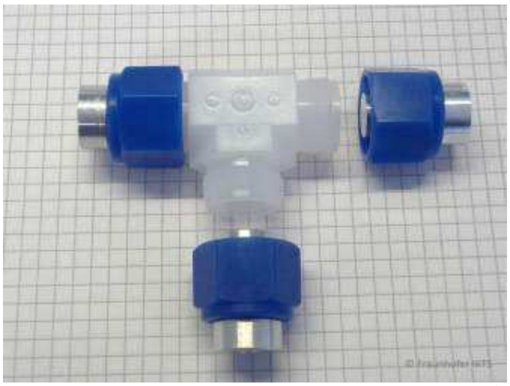
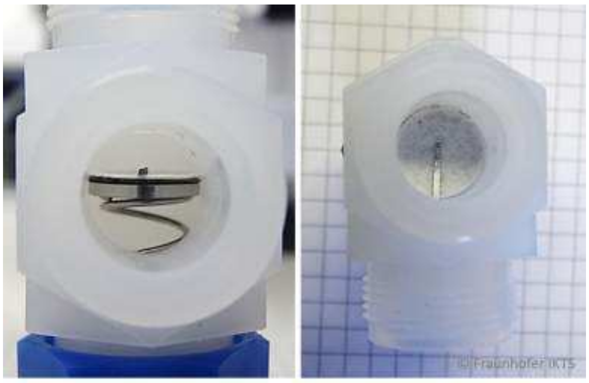
a) aluminium spacer
b) cathode
c) separator + electrolyte
d) anode
e) stainless steel spacer
f) lithium RE

IEC

Figure A.2 – Components of the electrochemical cell used for testing

The components of the cell are put into an argon-filled glove box to assemble the electrochemical package.

Construction steps are shown in Figure A.3.

Step	Figure	Description
1	 IEC	The warm cell components are pre-assembled up to the state shown left. Therefore the screw caps are pulled over the aluminium stamps. Afterwards one low and then one high gasket are raised at each stamp. Finally, one assembled closing is screwed on the cell body. The prepared parts and additional components are transferred into the glove box.
2		To prepare the RE, a narrow strip (approx. 1 mm to 1,2 cm length, 1 mm width) of lithium is cut off from the coil material. The strip is placed under a manual press and compressed to a thickness of about 0,1 mm, then manually cut to a width of about 0,5 mm.
3	 IEC	Step 1: A spring and the aluminium spacer are put into the pre-assembled cell body. Step 2: The cathode (punched out and dried under vacuum before) is placed on the spacer and wetted with 5 drops of the electrolyte, 1M $LiPF_6$ in 1:1 EC:DEC (for example, LP40). Step 3: One layer of glass fibre separator, which is punched out and dried under vacuum in advance, is placed onto the cathode and soaked with 3 drops of the electrolyte (LP40).
3	 IEC	The RE is placed on top of the separator. One end of the strip protrudes in the opening perpendicular to the cell main axis.

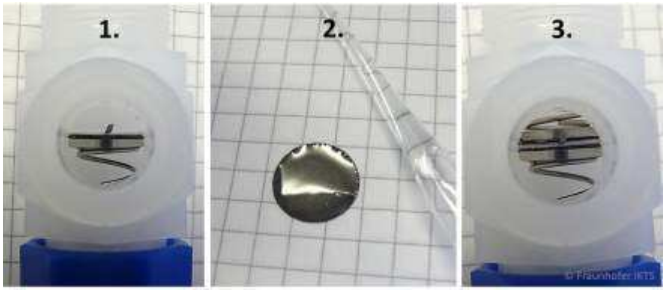
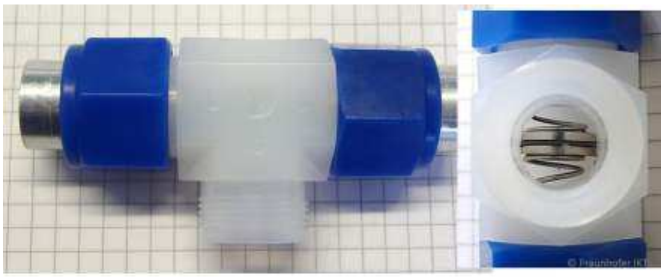
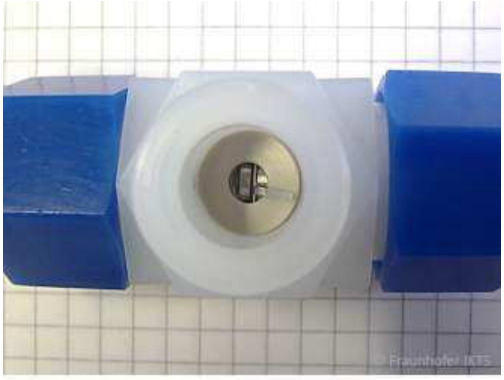
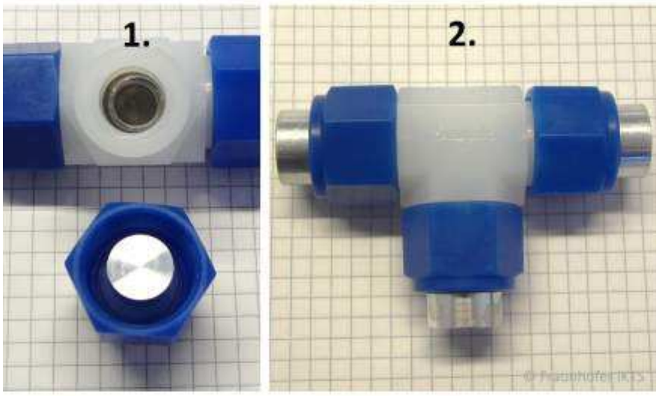
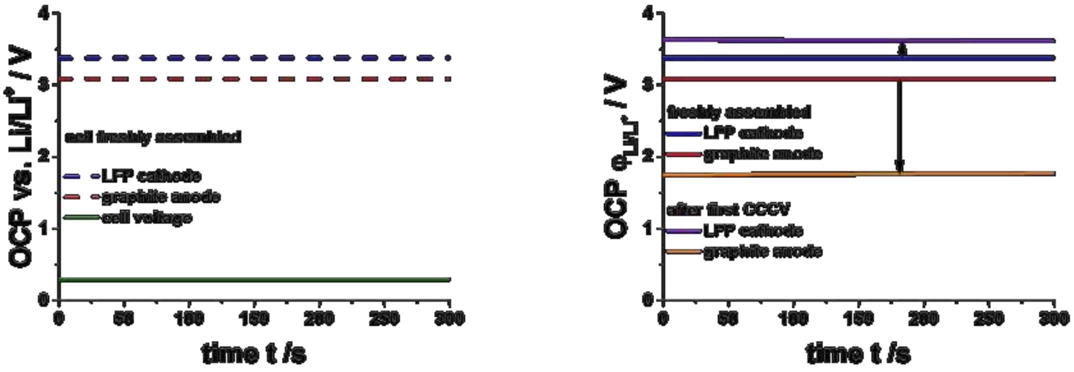
Step	Figure	Description
4	 *IEC*	Step 1: The second layer of glass fibre separator is placed on top of the sandwich and soaked with 3 drops of the electrolyte (LP40). Step 2: The anode (punched out and dried under vacuum before) is wetted with 5 drops of the electrolyte (LP40) outside the cell. Step 3: The soaked anode is put onto the separator. Afterwards a stainless steel spacer and a spring are placed above.
5	 *IEC*	The cell is closed by loosely tightening the screw caps at both openings along the cell main axis.
6	 *IEC*	The PEEK Spacer is placed in the opening of the RE. The protruding end of the RE is threaded through the opening of the PEEK spacer and slightly bent.
7	 *IEC*	Step 1: A stainless steel spacer is placed on the PEEK spacer. It contacts the RE which lies between both spacers. Afterwards a spring is inserted. Step 2: The third opening of the cell is closed by tightening the screw cap. Finally, the screw caps at the cathode and anode ending are pulled tight. The cell is tested within the glove box with a multimeter.

Figure A.3 – 3-electrode screw cell assembling steps

A.2 Results for a LFP electrode

A.2.1 Open circuit voltage/potential (OCV/P)

See Figure A.4.



a) Open circuit potential of LFP cathode and graphite anode for freshly assembled cell

b) Change of the open circuit potential of LFP cathode and graphite anode after first CCCV

During the first CCCV the state of strong de-lithiation of the anode has been achieved, which caused unusually higher anode potential against the lithium reference electrode.

Figure A.4 – Open circuit voltage/potential (OCV/P)

A.2.2 Electrochemical impedance spectroscopy (EIS)

See Figure A.5.

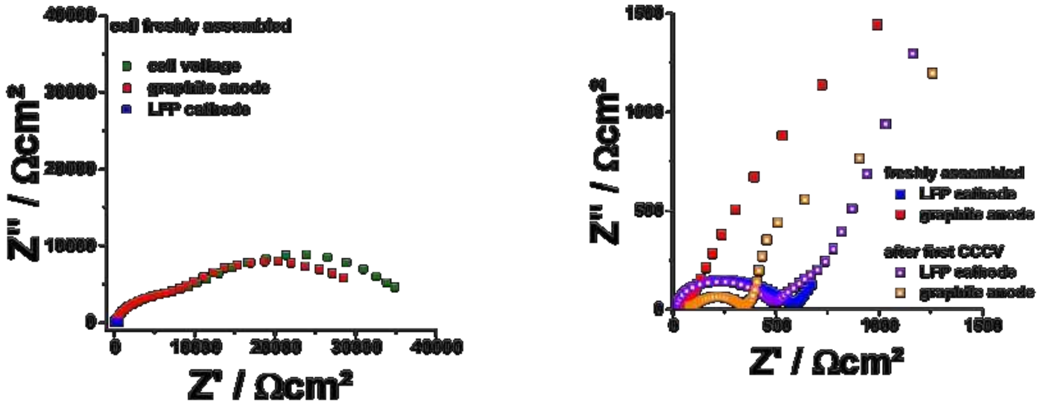
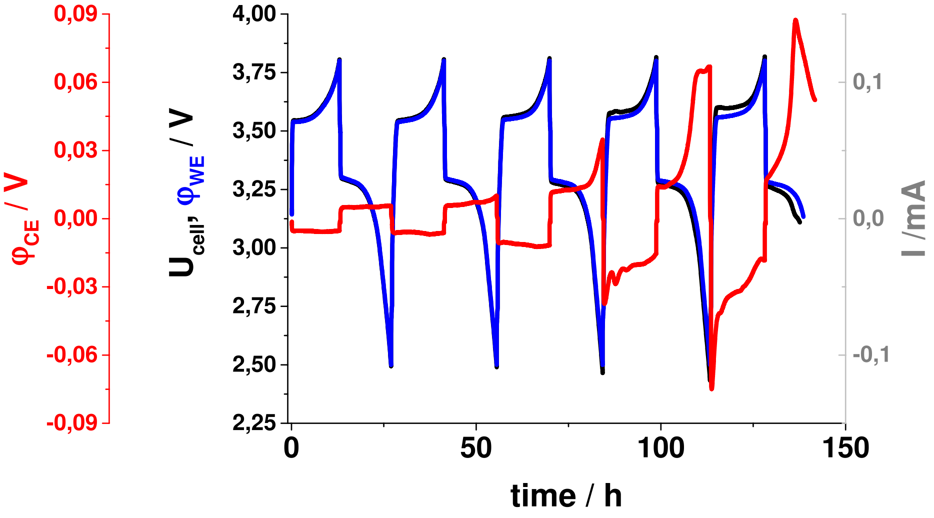


Figure A.5 – Electrochemical impedance spectra

A.2.3 Constant current constant voltage (CCCV/CC) charging-discharging

See Figure A.6.

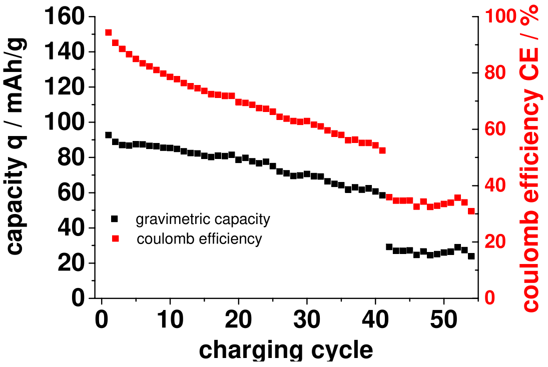


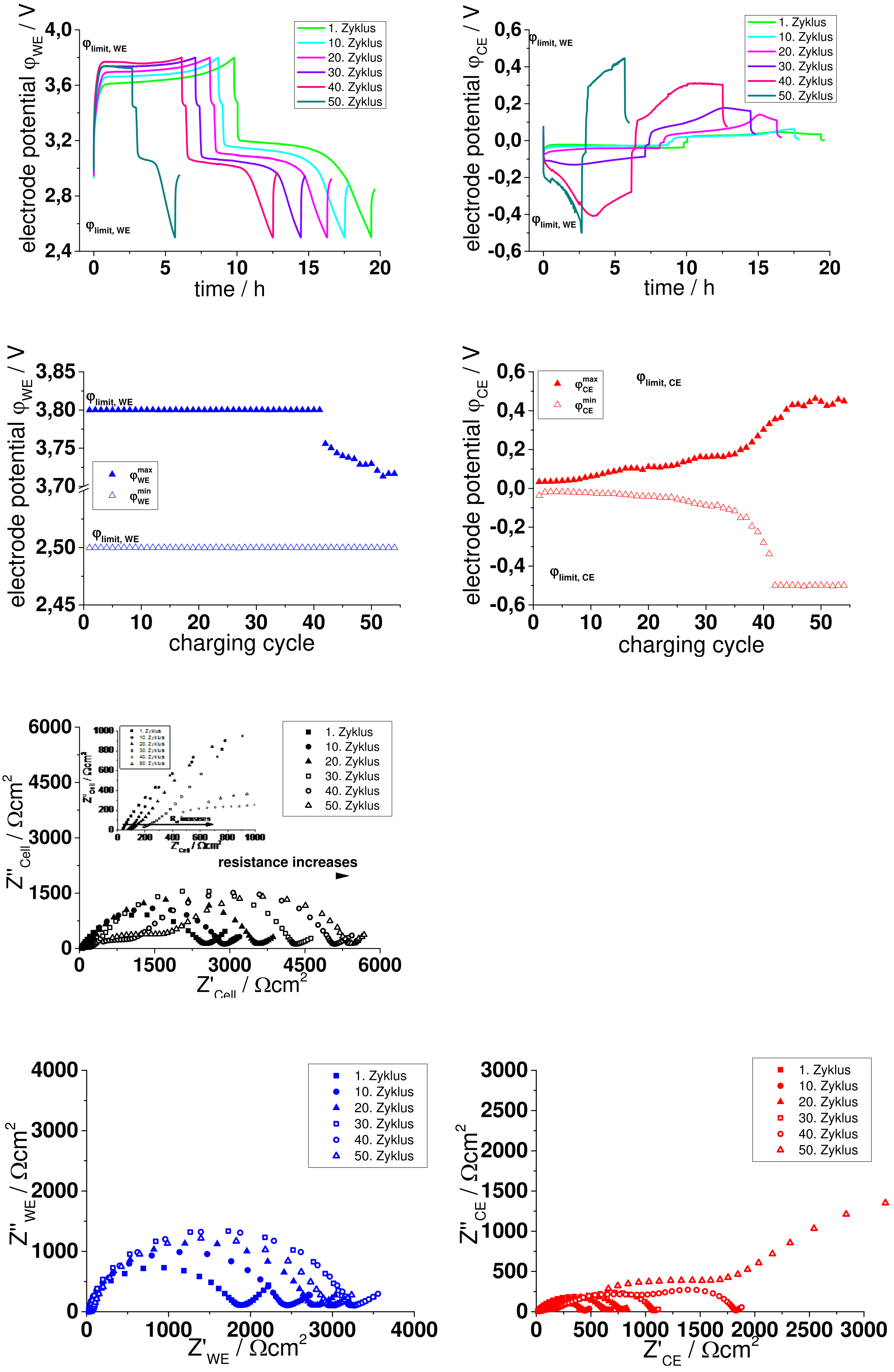
IEC

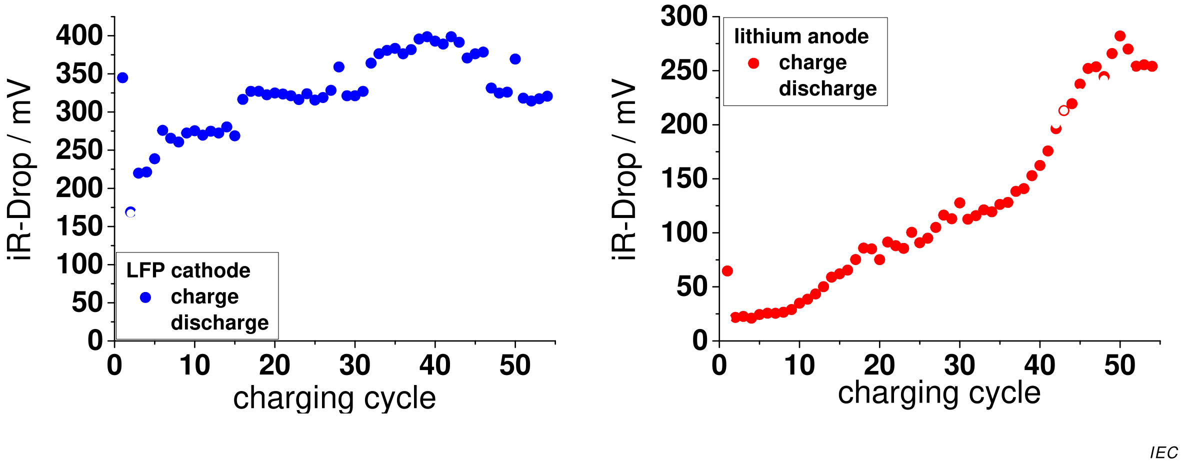
Figure A.6 – Constant current constant voltage (CCCV/CC) charging-discharging

A.2.4 Ageing tests

See Figure A.7.




electrode potential φ_WE / V
4,0
3,6
3,2
2,8
2,4
φ_limit, WE
φ_limit, WE
time / h
0
5
10
15
20
1. Zyklus
10. Zyklus
20. Zyklus
30. Zyklus
40. Zyklus
50. Zyklus
electrode potential φ_CE / V
0,6
0,4
0,2
0,0
-0,2
-0,4
-0,6
φ_limit, WE
φ_limit, WE
time / h
1. Zyklus
10. Zyklus
20. Zyklus
30. Zyklus
40. Zyklus
50. Zyklus
electrode potential φ_WE / V
3,85
3,80
3,75
3,70
2,50
2,45
φ_limit, WE
φ_limit, WE
φ^max_WE
φ^min_WE
charging cycle
0
10
20
30
40
50
electrode potential φ_CE / V
φ^max_CE
φ^min_CE
φ_limit, CE
φ_limit, CE
charging cycle
Z''_Cell / Ωcm²
6000
4500
3000
1500
0
Z'_Cell / Ωcm²
resistance increases
1. Zyklus
10. Zyklus
20. Zyklus
30. Zyklus
40. Zyklus
50. Zyklus
1000
800
600
400
200
0
Z''_Cell / Ωcm²
Z'_Cell / Ωcm²
R_ct increases
Z''_WE / Ωcm²
4000
3000
2000
1000
0
Z'_WE / Ωcm²
1. Zyklus
10. Zyklus
20. Zyklus
30. Zyklus
40. Zyklus
50. Zyklus
Z''_CE / Ωcm²
3000
2500
2000
1500
1000
500
0
Z'_CE / Ωcm²
1. Zyklus
10. Zyklus
20. Zyklus
30. Zyklus
40. Zyklus
50. Zyklus



NOTE "Zyklus" = "cycle".

Figure A.7 – Comparison of results of ageing tests using 3-electrode screw cell

INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

3, rue de Varembé
PO Box 131
CH-1211 Geneva 20
Switzerland

Tel: + 41 22 919 02 11
Fax: + 41 22 919 03 00
info@iec.ch
www.iec.ch