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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 4-1 Cathode nanomaterials for lithium ion batteries – Electrochemical characterisation, 2-electrode cell method

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

IEC 62607-4-1, 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
113/173/DTS	113/192/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 publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts of 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 publication will remain unchanged until the stability date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication 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- withdrawn,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.

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INTRODUCTION

The future utilisation 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 regarded as temporary solutions. From today's perspective, lithium-ion batteries and their derivative innovative concepts must be 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 lithium ion batteries is important for their customized development. This IEC technical specification provides a standard methodology which can be used to characterize the electrochemical properties of new cathode nanomaterials that will be employed in lithium ion batteries. Following this method will allow comparison of different types of cathode nanomaterial and comparison of the results of different research groups.

A revised edition 2.0 is already under preparation to introduce changes proposed by IEC SC 21A. The future edition may e.g. include the following changes:

- The title will be amended: the term “lithium ion batteries" will be replaced by “nano-enabled electrical energy storage”.
- The scope will be revised to change the phrase "lithium ion battery" to e.g., "lithium ion batteries utilizing lithium iron phosphate".
- The definition of "electrode nanomaterials" will be revised to be more specific, reading e.g. "electrode containing a nanomaterial portion of more than xx% by weight".

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 4-1 Cathode nanomaterials for lithium ion batteries – Electrochemical characterisation, 2-electrode cell method

1 Scope

This part of IEC 62607 provides a standardized method for the determination of electrochemical properties of lithium ion battery cathode nanomaterials to enable customers to:

a) decide whether or not a cathode nanomaterial is usable, and

b) select a cathode nanomaterial suitable for their application.

This technical specification includes:

– definitions of terminology used in this document,
– 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,
– case studies and
– references.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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, acronyms and abbreviations

3.1 Terms and definitions

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

3.1.1
cathode nanomaterial
electrodes used as cathodes in lithium ion batteries

Note 1 to entry: The cathode nanomaterial is a foil with a multilayered layout, built up 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 LCO, NCA, NCM, and LFP), a conducting phase (carbon black) and an organic binder (PVDF).

3.1.2
screw cell
cell providing the geometrical conditions in the two-electrode arrangement

Note 1 to entry: The electrochemical characterisation of the cathode nanomaterial is carried out in screw cells. The cell setup includes springs and metallic spacers and the electrode package with the anode, the separator impregnated with electrolyte and the cathode. For this purpose, various cell designs are possible. The case study in Annex A shows a cell design based on ½ inch PFA Swagelok fitting.[1] .

3.1.3
cell voltage
***U*cell**
difference of the electrochemical potentials of the cathode and the anode

3.1.4
cell resistance
***R*el**
ohmic internal resistance of the testing cell

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

3.1.5
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 oxidises 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 Acronyms and abbreviations

LCO: Lithium cobalt oxide $LiCoO_2$

NCA: Lithium nickel cobalt aluminium oxide Li(Ni, Co, Al)O_2

NCM: Lithium nickel cobalt manganese oxide $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

LFP: Lithium iron phosphate $LiFePO_4$

PVDF: Polyvinylidene fluoride

EC: ethylene carbonate

DEC: diethyl carbonate

PE: polyethylene

OCV: Open circuit voltage

4 Sample preparation methods

4.1 General

For the electrochemical characterisation of the cathode nanomaterial screw cells are used. The main aspects in preparation of these measuring cells are:

a) pre-treatment of the electrodes,

b) electing a proper electrolyte/ electrolyte volume, and

c) applying a defined and valid pressure on the electrode package.

[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.

4.2 Reagents

4.2.1 Cathode foil

The cathode material is put into an argon filled glove box immediately after preparation/ receiving to avoid contact to atmospheric moisture.

4.2.2 Anode

Metallic lithium is used as an anode material. The lithium foil (thickness d = 0,25 mm) should be unpacked in an argon filled glove box and then used as delivered.

4.2.3 Solvents and separator

The material testing should be carried out in an electrolyte of comparable composition. Currently $LiPF_6$-containing electrolytes are usually applied in commercial batteries. For the investigation commercial electrolyte of the type LP40 (1M LiPF6 in 1:1 EC:DEC) with a defined purity and water content < 5ppm or equivalent is recommended. Use of the alternative electrolyte is possible, however in this case the wettability of separator and electrode material by alternative electrolyte should be proven in separate tests. Viledon®[2], a PE-nonwoven by company Freudenberg, is the chosen separator material. Other separator material can also be used, however in this case the wettability of separator electrolyte should be proven in separate tests.

4.3 Pre-treatment of the cathode nanomaterial

The cathode foil is dried in a vacuum oven to achieve water contents of <100 ppm in the active material. Exemplary drying conditions are: T = 120 °C, p = 1 mbar – 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 <100 ppm 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 used in the Swagelok cell are punched out or laser cutted from the foil coated with cathode layer. The mass of the punched electrodes is determined by substracting the mass of uncoated foil from the mass of coated foil.

From the mass of the electrodes the theoretical capacity Q is estimated as follows:

$m_{Activ}=x^*(m_{Electrode}-m_{Substrate})$

$n_{Li}=m_{Activ}/M_{Activ}$ [mmol]

$Q = n_{Li}*F*z/3600$ [mAh] (z = 1, F = 96 485 C/mol)

$q_M= Q / m_{Electrode}$ [mAh/g]

$q_A=Q / m_{Activ}$ [mAh/g]

$q_F=Q / A$ [mAh/cm²]

For these calculations the following material data shall be given:

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[2] Viledon® is the tradename of a product supplied by Freudenberg Nonwovens. This information is given for the convenience of users of this standard and does not constitute an endorsement by IEC of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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

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

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 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 – 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 are mounted as shown in Clause A.1. Afterwards they are put into the glove box to assemble the electrochemical package under argon atmosphere. All materials under this section must be handled under argon atmosphere in a glove box. In the glove box the maximum O_2 content is 50 ppm and the maximum H_2O content is 10 ppm.

The cathode is placed inside the cell body and impregnated with LP40 electrolyte (5 drops, for cell area 1,27 cm^2 and cathode thickness of 50 μm).

The separator with thickness of 190 μm is punched out and 2 layers are placed onto the cathode. A defined amount of LP40 electrolyte (300 mg or 5 drops dispensed from micropipette per separator layer) is put on the separator.

The lithium anode is punched out and mechanically pressed onto a stainless steel or titanium spacer to minimize contact resistance. Afterwards it is put on the separator. By use of stainless steel spacers the corrosion free spacer operation should be proven after disassembling the cell. Stainless steel spacers should be replaced by titanium spacers if corrosion is observed.

Finally the cell body is equipped with the stainless steel spring (k = 2,87 N/mm) and a valid number of stainless steel spacers, and the cell is screwed under pressure.

Table 1 – Spring force and pressure

	Spring	Spring + 1 spacer	Spring + 2 spacer	Spring + 3 spacer
Spring force / N	14,87	19,23	23,59	27,95
Pressure / kNm^{-2}	117	151	186	220

A brief function test is performed by determining the cell voltage with a multimeter:

U = (3 ± 0,5) V (specific value of the materials) → correct

U < 1,6 V → fail

In case the OCV of the cells with the same type of the cathode is between 1,6 and 2,5 V, such cells can be cycled for 5 to 10 times. If the discharge capacity of the electrode is <35 % of theoretical capacity Q (<0,35*Q, see 4.3) or strong degradation (>50 % after 10 cycles or >10 % / cycle after 3rd cycle) of capacity is observed the results should be disregarded and the sample preparation optimized.

4.5 Disassembly of the screw cell

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

The used cell components have to be stored and disposed of in conformity with 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 and reference electrode. 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 voltage (OCV)

5.2.1 Demarcation of method

The open circuit voltage of an electrochemical 2-electrode cell is the potential measured in currentless state. It can be considered equivalent to the open cell potential.

5.2.2 Experimental procedures and measurement conditions

The cell is connected to a potentiostat by banana jacks. The OCV is detected over 5 min; stabilisation of the value should be verified. For common cathode materials the value is set in the range of (3 ± 0,5) V (see also 4.4).

5.3 Potentiostatic electrochemical impedance spectroscopy (EIS)

5.3.1 Demarcation of method

Electrochemical impedance spectroscopy is the method of measurement of complex impedance of the cell using periodically oscillating voltage for resolving 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. The EIS measurement is performed under the conditions given below:

DC = OCV

AC = 10 mV

f = 100 kHz – 0,01 Hz

The internal ohmic resistance R_{el} corresponds to the real part of impedance at the highest frequency R_{real}(100 kHz). If R_{real}(100 kHz) < 20 Ω, the cell is suitable for charge discharge experiments. Otherwise a new cell should be manufactured.

5.4 Charge discharge experiment (constant current constant voltage, CCCV)

5.4.1 Demarcation of method

The constant current constant voltage method is a method of battery charge/discharge where at first galvanostatic (CC) cell control is applied and at the end the potentiostatic cell control (CV) is used for charging / discharging.

5.4.2 Experimental procedures and measurement conditions

The cell is connected to a potentiostat as described in Chapter 5. The potential and current limits of the CCCV procedure depend on the cathode material, the values below being valid for LCO, NCA and NCM cathodes:

a) I_{charge} = 0,1 C (0,1 C = Q/10) with C – discharge capacity of the electrode
b) $U_{upper\ limit}$ = 4,2 V
c) $t_{potstat}$ = 3 600 s (1 h)
d) I_{limit} = 0,01C (10 % of I_{charge})
e) $I_{discharge}$ = –0,1 C
f) U_{limit} = 2,5 V
g) 10 cycles

For LFP cathodes, the higher voltage limits are lower due to the lower open circuit voltage obtained using this material:

h) $U_{upper\ limit}$ = 3,8 V

6 Data analysis / Interpretation of results

6.1 Open circuit potential

a) Calculation: None
b) Chart: voltage vs. time (see Clause A.2, Figure A.4)
c) Target value: cell voltage = stable open circuit potential

6.2 Electrochemical impedance spectroscopy

a) Calculation: Z_{real}/Z_{imag} normalised: $Z^*A = Z_{norm}$ [Ωcm²]
b) Chart: "Nyquist-Plot" -Z_{imag} vs. Z_{real} (see Clause A.2, Figure A.5)
c) Target value: internal resistance R_{el} = Z_{real}(at 100 kHz) (see Clause A.2, Figure A.6)

6.3 Constant current constant voltage (CCCV) charging-discharging

a) Calculation: I normalised: $i = I/A$ [mA/cm²]
sum of measuring times: $t_{ges} = t_{step1} + t_{step2}$ …+t_{stepN} [s]
capacity q_F: integration $q_F = \int idt$
mass capacity q_A: $q_A = q_F * A/m_{Aktiv}$ [mAh/g]
b) Chart: CC-CV-diagram: U vs. t and i vs. t (see Clause A.2)
capacity development: q_A/q_F vs. number of cycles
c) Target value: discharge capacities q_F and q_A
IR-drop ΔU
IR-drop is defined as a voltage change (ΔU) during switching between charging mode ($I \neq 0$ mA) to discharging mode (OCV value at I = 0 mA) during CCCV procedure.

Annex A
(informative)

Case study

A.1 Sample preparation

Components for the cell are shown in Figure A.1.

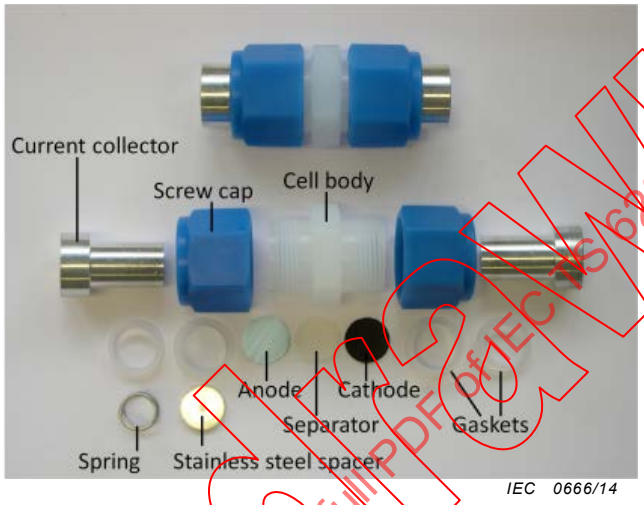


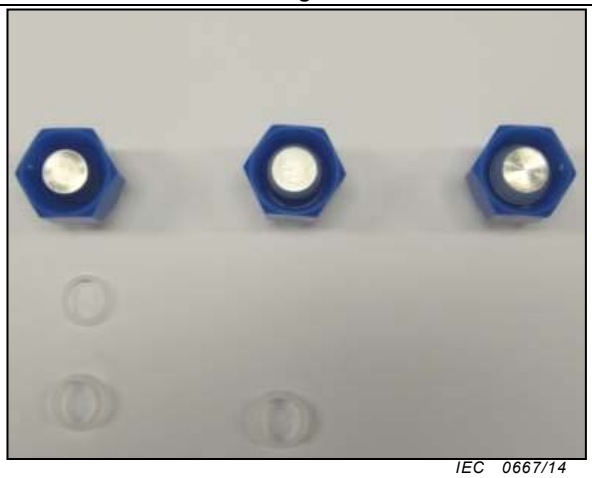
Figure A.1 – Components for the cell

Components which are required:

– 1 cell body (*inner diameter = 1,27 cm, outer diameter = 2,53 cm)*;
– 2 aluminium current collectors;
– 2 screw caps;
– 2 low gaskets;
– 2 high gaskets;
– 2 stainless steel spacer;
– 1 cathode;
– 2 separators;
– 1 anode;
– 1 spring;
– electrolyte.

The warmed up components of the cell are put into a glove box to assemble the electrochemical package under argon atmosphere.

Construction steps are shown in Figure A.2.

Step	Figure	Description
a	 IEC 0667/14	The screw cap is pulled over a current collector, afterwards first the low gasket and then the high gasket are raised at the current collector.
b	 IEC 0668/14	The cell body is screwed onto the screw cap.
c	 IEC 0669/14	The cathode is punched out with an area of 1,27 cm² and put onto the current collector. The cathode with thickness of 50 µm is impregnated with a defined amount of LP40 electrolyte (300 mg or 5 drops dispensed from a micropipette).

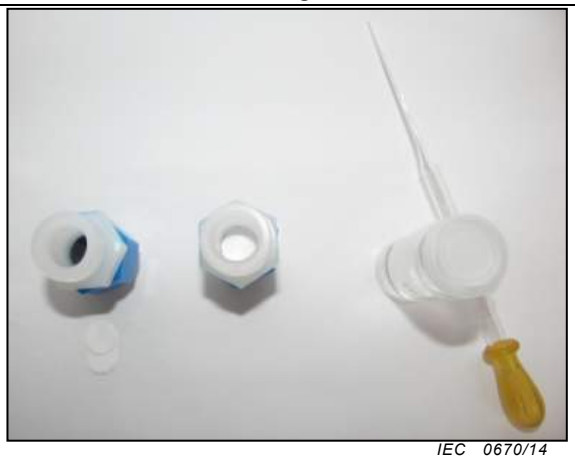
Step	Figure	Description
d	 IEC 0670/14	Two separators with thickness 190 μm are positioned at the cathode and impregnated with 10 drops of electrolyte.
e	 IEC 0671/14	As anode, lithium metal foil is punched out and pressed onto a stainless steel spacer to minimize contact resistance.
f	 IEC 0672/14	The lithium anode is placed onto the separator inside the cell body, then the spring is introduced.
g	 IEC 0673/14	The second stainless steel spacer is placed on the spring and the screw cap is screwed onto the cell body.

Figure A.2 – Construction steps (a to g)

A.2 Results for a LCO electrode

Results for a LOC electrode are shown in Figures A.3 to A.6.

Figure A.3 presents the results of open circuit voltage/potential (OCV/P).

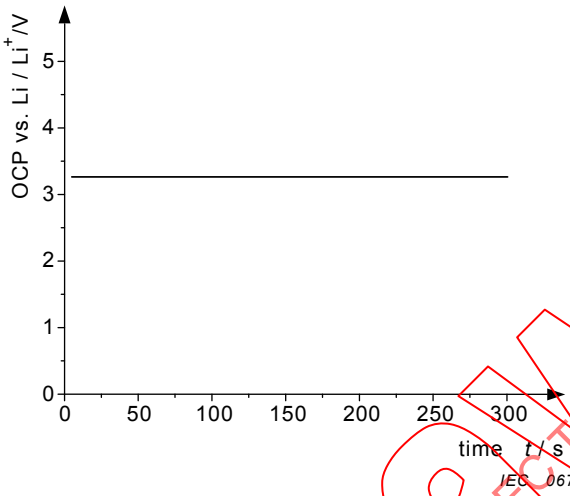


Figure A.3 – Open circuit voltage/potential time graph

Figure A.4 presents the results of electrochemical impedance spectroscopy (EIS).

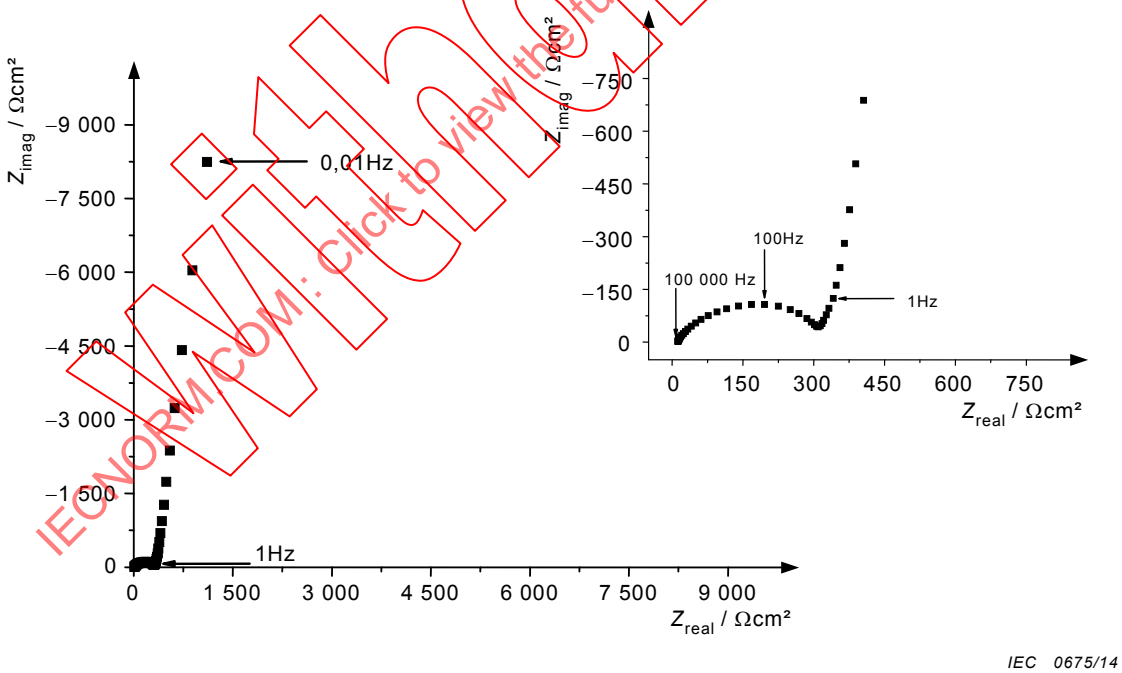


Figure A.4 – Electrochemical impedance graph