Lithium Batteries for Second Use

EURAMET

Publishable Summary for 17IND10 LiBforSecUse Quality assessment of electric vehicle Li ion batteries for second use applications

Overview

Li-ion batteries have useful applications ever after removal from their first use in electric vehicles, such as low-cost energy storage media in conjunction with photovoltaic systems. However, their uptake is hampered by the lack of accurate and cost-effective characterisation techniques. This project has developed robust measurement procedures and paved the way for a supporting metrological infrastructure to measure the residual capacity of li-ion batteries using fast and non-destructive impedance-based methods and investigate the feasibility to predict premature failure. Such procedures will enable the economical and sustainable re-use of the multitude of Li-ion batteries, which become more and more available in the meanwhile.

Need

Once Li-ion batteries have reached their end of life in an electric vehicle (EV), these batteries can be used for many years in a wide range of applications. For instance, they can be used as reserve power in electricity grids or for local energy storage in conjunction with photovoltaic systems. Such batteries are called second-use (or second-life) batteries. 8.5 million electric vehicles were globally sold until 2020. It is estimated that up to 150 million second-use batteries will be available by 2030. The sale of repurposed batteries could therefore provide considerable economic opportunities for the European market, and it would improve the environmental footprint of electric vehicle Li-ion batteries.

Hence, the optimisation of battery reprocessing is urgently required, otherwise, the application of second-use batteries will be too expensive to be economically viable. In particular, validated impedance-based procedures to measure the residual capacity need to be significantly faster and more accurate compared to existing methods. Furthermore, a robust measurement procedure to assess the risk of premature failure, at least qualitatively, does not yet exist. Impedance-based measurement and evaluation methods could serve this purpose however, the underpinning metrological framework, including traceability, quantified measurement uncertainties and defined measurement procedures in order to guarantee comparability of the results, is currently lacking. Consequently, standardised protocols for life cycle testing and impedance measurements as well as practical calibration concepts and standards for impedance measurement devices must be developed. In the broader, environmental context, the EU has declared the need to reduce greenhouse gas emissions on several occasions. Hence, actions to implement second-use batteries in conjunction with renewable energy sources need to be supported, instead of wasting enormous amounts of storage capacity and buying new storage systems, primarily imported from Asia, for that purpose.

Objectives

The overall objective of this project was to establish an accurate, fast and practical measurement procedure for European industry to measure the residual capacity and to study feasibility to detect premature failure of Li-ion batteries of electric vehicles (EVs) for second use applications using impedance based methods. The specific objectives of the project were:

1. To develop protocols for life cycle testing of different types of Li-ion- battery cells and modules in terms of capacity, chemistry and geometry, at different temperatures, currents and cycling patterns. The life cycle tests will include both impedance-based methods (e.g. EIS, EC, DRT, NFRA and TDM) and conventional methods e.g. open circuit voltage (OCV) measurement and current integration.
2. To develop validated impedance-based measurement procedures to measure the residual capacity of Li-ion battery cells and modules with a target relative uncertainty of better than 3 %. In addition, to assess the feasibility of detecting the premature sudden death of Li--ion batteries based on impedance-based measurements.

3. To establish traceable impedance measurements in the mΩ and sub-mΩ range in the full complex plane in the frequency range between 10 mHz and 5 kHz, with a target relative uncertainty of 1 %. This will include the development of low impedance standards with arbitrary phase angles and a calibration method for impedance meters.
4. To develop a validated protocol for the application to Li-ion battery modules of the traceable impedance measurements in the mΩ and submΩ range in the full complex plane in the frequency range between 10 mHz and 5 kHz.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. batteries manufacturers and the automotive industry) standards developing organisations (e.g. IEC-TC21 and input to IEC 62660-1) and end users (e.g. the transport sector).

Progress beyond the state-of-the-art

Impedance-based measurement methods depend on precisely applied tests and measurement conditions. In the past, several life cycle tests (LCTs), including impedance-based measurements, have been performed to investigate Li-ion batteries. Unfortunately, those tests were lacking a common metrological basis, so reproducibility and comparability of the results cannot be assured. Consequently, results were often deemed inconsistent or insignificant. In order to overcome this shortcoming, the project developed various impedance measurement methods and conventional methods which have been reviewed, tested and agreed upon among the project partners.

At present, battery conditions such as capacity and power are conventionally measured by integrating the current of a complete charge or discharge of the battery and by measuring battery voltage curves under defined conditions. These methods do not fulfil the requirements for quality assessment of second-use batteries since they are either too slow or too inaccurate for economically viable reprocessing of Li-ion batteries. Hence, an adequate measurement procedure is lacking and, measurement procedures for assessing the risk of accelerated failure do not exist. This project established impedance-based measurement procedures for this purpose. More specifically, sets of metrologically consistent impedance-based measurement results have been established for the first time, which are based on life cycle tests of different types of Li-ion battery cells under various cycling conditions. The partners have investigated the results of a set of impedances measured under repeatability conditions with various impedance-based evaluation methods. Ageing parameters have been derived from the data set. Based on this investigation, new impedance-based measurement procedures to measure the residual capacity of high-energy Li-ion battery cells and modules with a target relative uncertainty of better than 3 % have been developed and the feasibility of using them to detect disadvantageous accelerated ageing of Li-ion batteries will be investigated.

Such impedance-based methods require sound metrological specifications to provide meaningful results. Up to now, there has been no metrological basis for the calibration of impedance measurement devices in the low impedance (mΩ) range. Adequate impedance standards and associated measurement uncertainties, as well as calibration procedures and the required metrological calibration infrastructure, have been missing. This project has gone beyond the state of the art by defining and validating respective measurement procedures for Li-ion battery cells and modules, and by developing and characterising adequate low-impedance standards with arbitrary phase angles, also refining impedance simulators developed in EMRP project SIB53 AIM QuTE.

Furthermore, the characterisation of Li-ion battery cells for second-use application using impedance-based methods has neither been considered for standardisation nor have the related metrological principles been realised in corresponding industrial measurements. Hence, uptake of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. batteries, manufacturers and the automotive industry), standards developing organisations (e.g. IEC-TC21, IEC 62660-1) and end-users (e.g. the transport sector) will be facilitated.

Results

Objective 1 - Metrologically sound life cycle test and impedance measurement procedures

Metrologically sound measurement procedures for life cycle tests of Li-ion batteries and associated impedance measurement procedures have been developed, validated, and published as a good practice guide. In addition, an uncertainty budget for respective impedance-based measurements has been developed. Applying the procedures, a series of life cycle tests have been completed by several institutes to assess the reproducibility of the results, validate the procedures, and investigate the robustness of the models developed to address objective 2. As an outcome of objective 1, a large database of metrologically consistent impedance-based measurement results in dependence of the age of Li-ion cells has been available to address objective 2.

Objective 2 - Development and characterisation of impedance-based procedures to measure the residual capacity and detect accelerated aging

Impedance results measured under reproducibility conditions have been investigated with different kinds of impedance-based evaluation methods. Ageing parameters have been identified based on a statistical correlation model that has been adapted for this purpose. The impedance-based evaluation methods have finally been used to develop four empirical models to predict the residual capacity, i.e. direct impedance evaluation, equivalent circuit fitting, analysis of distributed relaxation times and analysis of non-linear frequency response. Each of the models had pros and cons concerning its application. However, they have proven to be consistent and have shown equivalent ability to predict the residual capacity. A statistical assessment of the predicted residual capacity has shown a mean deviation smaller than 1.5 % from the actual capacity if the models are applied to the impedance data used for model development. The robustness of the models has been validated with the data from additional life cycle tests measured with varying cycling conditions, revealing an increase of the deviation up to 5 %. After optimising the models, the mean deviation was smaller than 3 %, complying with the target value. The results have been summarised in a publication submitted to a peer-reviewed journal of high impact. The methodology has been published as a good practice guide. The robustness has further been substantiated by a comparison measurement, confirming the target uncertainty. Several techniques for post-mortem analysis have been applied to fresh and to aged cells taken from the life cycle tests. Furthermore, physicochemical simulation models have been conducted. Both activities aimed to get a deeper insight into the ageing mechanism of the investigated cells and to substantiate the empirical models. However, time constraints, mainly imposed by the Covid-19 pandemic, have eventually prevented a systematic evaluation of the post-mortem and simulation results during the runtime of the project, so the evaluation has remained qualitative.

Objective 3 - Low impedance standards and calibration procedures

Various low-impedance standards have been developed (current shunt, reactance standard with bias, passive standard with non-zero phase angle, impedance simulator). Furthermore, a digital impedance bridge has been developed that can be used to characterise low-impedance standards in the mW range. A good practice guide on the calibration of impedance measurement devices and a good practice guide on low-impedance measurements have been created and published. These activities aimed to pave the way for a metrological sound infrastructure for traceable impedance measurements in the mΩ and sub-mΩ range, with the full complex plane in the frequency range between 10 mHz and 5 kHz, and a target relative uncertainty of 1%. Comparison measurements on the characterisation of impedance standards, impedance meter calibration and low impedance measurements have been conducted to validate the standards and the measurement procedures. An equivalence far better than 1% has been achieved in the relevant frequency range demonstrating the usability of the developed standards and procedures.

Objective 4 - Validated test protocol to characterise modules based on impedance measurements

A respective measurement protocol has been developed, and at least one of the empirical models has been applied to modules. It has been qualitatively evaluated with the impedance spectra of a life cycle test of four modules, also including the impedance spectra of the individual cells. The usability was demonstrated, even though the uncertainty of the spectra of the modules was relatively large compared to that of the individual cells of the modules. However, due to time constraints, imposed by the Covid-19 pandemic, the residual capacity of the modules couldn't be decreased to values relevant for second-use batteries (70 – 80 % of the fresh cell capacity). Nevertheless, it must be emphasised that such an approach has been applied to modules for the first time. The preliminary evaluation was promising.

Impact

The project presented at least 11 papers at various national and international conferences and workshops, such as the International Metrology Congress, COMSOL Conference, PRiME meeting of the Electrochemical Society, MoD Val, International Symposium on Electrochemical Analysis, Advanced Battery Power, Circusol workshop 2019, Battery reuse solutions seminar, Tulevaisuuden Akku ecosystem (a national workshop in Helsinki). Two of these workshops have been organised by the consortium. The presentations were aimed at representatives from industry and the scientific community. The project objectives and its progress have also been presented at relevant technical committee meetings of EURAMET (TCMC-SCEA/Bern 2020, TCEM-

SCLF/Ljubljana 2019, TCMC-SCEA 2021 (online)) and the Electrochemical Working Group of the Consultative Committee for the Amount of Substance at the International Bureau for Weights and Measures (BIPM, 2021, online). Eight peer-reviewed, open access papers have been published and one submitted. The latter is an invited review paper on the impedance spectroscopy of commercial Li-ion cells in the highly recognised Journal of Power Sources.

Impact on industrial and other user communities

This project has, for the first time, realised SI traceability for mΩ and sub-mΩ impedance measurement results in the complete complex plane with a target uncertainty of less than 1%. Manufacturers of impedance measurement devices and end-users from industry and research institutions will be able to calibrate the devices to provide traceability to the SI in this challenging impedance range. Furthermore, the published calibration procedure will help end-users to identify and correct systematic measurement errors. As a result, the low impedance measurements in industry and research facilities; especially for Li-ion- batteries; will be more accurate and reliable.

In addition, by providing new and metrologically sound measurement procedures based on impedance measurement and evaluation methods, the characterisation of Li-ion battery cells and modules will be significantly accelerated in comparison to the current practice. Once established, the new procedures will enable test centres and companies to effectively test or reprocess Li-ion batteries for second-use applications and take fast and reliable measurements for residual capacity. Subsequently, these improvements will facilitate the development of economically viable business models for the reuse of Li-ion batteries salvaged from electrical vehicles. Furthermore, the preliminary results of a feasibility study investigating the potential of impedance-based measurements to predict premature accelerated ageing are promising. It might be possible to develop a method in future to detect if premature failure of second-use batteries has to be expected.

Impact on the metrology and scientific communities

This project has paved the way for primary calibration services in an impedance range that has not been covered so far in the metrological services provided by National Metrology Institutes (NMIs). It will provide a basis for pilot studies and key comparisons in relation to low impedances at arbitrary phase angles at the relevant technical committees and working groups of EURAMET and the respective consultative committees of the BIPM. Corresponding entries in the databases of the Calibration and Measurement Capabilities of NMIs will be prepared. This objective has been presented at the EURAMET TC-EM and the EURAMET TC-MC meetings. The first comparison measurement on impedance measurements of Li-ion batteries has been approved by EURAMET TC-MC.

Furthermore, the identification and metrological validation of reproducibility conditions for impedance-based measurement methods and life cycle tests of Li-ion battery cells and modules will provide a sound metrological basis for these measurements. This will significantly improve their accuracy and increase confidence in a measurement method that has unrivalled potential to provide information about the internal processes of Li-ion batteries in a non-destructive measurement. Unfortunately, up to now, this method has been deemed to provide unreproducible and ambiguous measurement results. The guides published by this project will overcome this situation and will provide a common basis to make impedance measurements accepted as a fast and reliable tool in Li-ion- battery characterisation and research.

Eventually, results of 13 LCTs on 34 cells, with more than 6000 impedance data sets and corresponding capacity measurements have been created. The results have been made publicly available on the LiBforSecUse repository for further use by external users, with a steady increase of observed downloads (41 downloads by the time this report was submitted).

Impact on relevant standards

The consortium was involved in the development of new standards and guides under IEC TC 21/PT 63330 'Requirements for reuse of secondary batteries and IEC SC 21A/PT 63338 'General guidance on reuse and repurposing of secondary cells and batteries, which are currently in the committee draft stage. These documents were improved as a result of this project. Currently, the impedance-based methods to predict residual capacity are in a laboratory stage, not ready for direct practical use. However, once optimised for practical use, a new work item will be raised within IEC TC 21/JWG 69 Li leading to standardisation. First steps have been taken to establish traceability of low-impedance standards and measurements within the framework of the CIPM-MRA at EURAMET and respective consultative committees and working groups of the BIPM (i.e. in technical committees related to electrochemical and low-frequency, electrical measurements).

Longer term economic, social and environmental impacts

The energy supply in Europe is currently undergoing a dramatic transition from fossil fuels to renewable energy sources for several reasons. The most relevant renewable energy sources, wind and sun, are not permanently available. Therefore, reliable energy storage systems need to be established. Li-ion battery technology is one of the most important candidates to comply with the demands for such systems. In particular, the use of second-use batteries for this purpose would provide significant economic impact in the production of Li-ion batteries. The outcomes of this project will contribute to creating the necessary conditions to establish a market for second-use batteries salvaged from EVs. It has provided new metrologically sound measurement procedures to make the measurement of residual capacity significantly more efficient in terms of measurement time. The large amount of battery energy storage capacity that will come to the end of its EV life in the years ahead will either be recycled or repurposed for second-use applications. If recycled (or even worse incinerated as is often the current practice), new batteries will have to be imported from outside Europe for applications such as storage of intermittent renewable energy sources, since there is no relevant battery production facility in Europe. In contrast, a vibrant European second-use market for batteries from EVs would decrease costs for such systems and the investment capital would remain in Europe. Moreover, the life cycle impact of renewable energy systems would be significantly improved and would contribute to achieving the climate and air quality goals declared by the European Union.

The main social impact of the increase in uptake of EVs and second use applications of Li-ion batteries will be the increase in quality of life and health of European citizens due to improved air quality and reduced noise pollution. This will also manifest itself in reduced strain on health services, less need for regular cleaning of buildings. It is also anticipated that an increase in social awareness of electromobility will result from the increased visibility of both EVs and second-use applications as this new market develops.

List of publications

1. Nina Meddings, et al, “Application of electrochemical impedance spectroscopy to commercial Li-ion cells: A review, Journal of Power Sources”, 2020, https://doi.org/10.1016/j.jpowsour.2020.228742
2. Jože Moškon et al ‘A Powerful Transmission Line Model for Analysis of Impedance of Insertion Battery Cells: A Case Study on the NMC-Li System’, J. Electrochem. Soc., 2020, https://doi.org/10.1149/1945-7111/abc769
3. Mašláň, Stanislav, “High capacitance simulation using mutual inductors”, Proceedings of the 24th IMEKO TC4 Symposium, 2020 http://doi.org/10.5281/zenodo.4630725
4. Mašláň, Stanislav. (2020) ‘Design of digital sampling impedance bridge for battery impedance spectroscopy’, Proceedings of the 24th IMEKO TC4 Symposium, http://doi.org/10.5281/zenodo.4630641
5. Klement Zelič, et al ‘Derivation of Transmission Line Model from the Concentrated Solution Theory (CST) for Porous Electrodes’, J. Electrochem. Soc, 2021, https://doi.org/10.1149/1945-7111/ac1314
6. Tanja Vidaković-Koch, et al, ‘Nonlinear Frequency Response Analysis: A Recent Review and Perspective’, Current Opinion in Electrochemistry, 2021, https://doi.org/10.1016/j.coelec.2021.100851
7. Benyamin Rusanto et al, ‘Primary measurement method for the characterisation of impedance standard in the mΩ range, Measurement Science and Technology’, 2022, https://doi.org/10.1088/1361-6501/ac6a45

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	01 September 2018, 42 months	
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Internal Funded Partners: 1 PTB, Germany 2 CMI, Czech Republic 3 LNE, France 4 METAS, Switzerland 5 NPL, UK 6 RISE, Sweden	External Funded Partners: 7 Aalto, Finland 8 ACE, UK 9 NIC, Slovenia 10 TUBS, Germany (withdrawn from 31/3/2022) 11 KIT, Germany	Unfunded Partners: 13 BRS, Germany 13 HIOKI, Japan 14 JRC, Europe 15 Li.plus, Germany
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