In-situ and operando Scanning Probe Facility for the study of redox processes on nanometer scale in Lithium Ion batteries

- First measurement results for in situ and operando characterisation of Lithium Ion Batteries by AFM techniques -

Walter Legerstee [1)] **Erik Kelder** [2)]

1) Rotterdam University of applied sciences

Department of engineering and Applied sciences, Section Automotive, Netherlands

2) JTechnical University Delft, Reactor Institute Delft, Storage of electrical energy, Netherlands

Presented at EVS 31 & EVTeC 2018, Kobe, Japan, October 1 - 3, 2018

ABSTRACT:

We developed a dedicated Atomic Force Microscopy set-up in a hermetically closed environment, coupled with a Galvanostat/Potentiostat which will be able to perform in-situ and operando measurements at the cathode-electrolyte and anode-electrolyte interface to monitor the interphase processes. The setup was tested in first measurements to prove the abilities for monitoring changes in morphology, impedance, and performing a combination of AFM-SECM for operando monitoring redox processes.

First results of operando Atomic Force Microscopy will be presented in this paper to indicate the possibilities of the new build facility for visualising the forming of the Solid Electrolyte Interphase (SEI), which proved to be responsible for the most important ageing meganisms, and thus the cycle and calendar life of the battery.

The measurements proved the possibilities of the setup to monitor SEI processes operando and visualizing impedance distribution on cathode-electrolyte and anode-electrolyte interfaces.

KEY WORDS: Operando measurements, Lithium Ion Batteries, Atomic Force Microscope, Local Impedance measurements, Solid Electrolyte Interface,

1. INTRODUCTION

As a result of practical requirements for automotive applications and the need for faster charging solutions, a large difference in charge moments and charge capacities is offered in order to charge vehicles. Fast charging becomes more common and contact-less charging is around the horizon. Resent insights show that wide variations in charging conditions lead to battery degradation which results in faster ageing[(1)]. Modelling these ageing processes and their relation with charge capacity makes it possible to introduce age-sensitive charging strategies. Battery algorithms can be expended with dynamic charge parameters allowing battery management systems to choose a charging strategy depending on the state of the battery, state of charge and state of health. The expected behaviour of the aged battery cells on charging circumstances will determine the applied strategy.

At the interface between cathode and electrolyte important battery ageing processes take place. In this so called Solid Electrolyte Interphase (SEI), the charge-transfer between cathode- and electrolyte ions causes impedance, which is related with processes that are responsible for capacity loss[2]. The capacity loss consists of a reversible and an irreversible part, both contributing to the impedance of the interphase. With impedance spectroscopy it is possible to locate these processes and to discriminate between the contribution of reversible and irreversible processes, but the relation of the irreversible processes with charging conditions is still difficult to understand.

In order to be able to investigate these processes, a combination of Atomic Force Microscopy (AFM), Electrochemical Impedance Spectroscopy (EIS) and Scanning ElectroChemical Microscopy (SECM) is being developed with which in-situ and operando research can be carried out. This technique will give insights in the contribution of the various SEI processes to the ageing of the battery and the relation of these processes with charging properties. The required data will be further analysed with model simulations, which makes it possible to derive quantitive information about interfacial charge transfer.

2. In-Situ and Operando AFM/SECM Set-up and dedicated Glovebox environment

2.1. Atomic Force Microscopy and Scanning Electrochemical Microscopy

Atomic Force Microscopy (AFM) is a high resolution Scanning Probe Microscope technique which makes it possible to study surface morphology on nanometer scale[5].

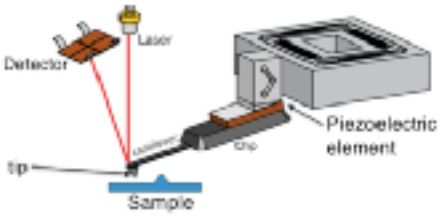


Figure 1: Principle of Atomic Force Microscopy

Figure 1 shows the principle of AFM where a nano needle scans the surface and the movements of the needle are detected by a laser signal. AFM can be merged with nano scale impedance measurement techniques which makes it possible to study in-situ and operando electrochemical processes in relation to morphologic information of the surface[9]. Figure 2 shows the principle of the impedance measurement with AFM. The nano needle scans the surface to generate a morphological image of the surface with a resolution between 1 and 30nm. The generated image is used to locate the regions of interest where nano impedance spectroscopy measurements can be carried out both on the surface as well as at several distances (nm scale) from the surface.

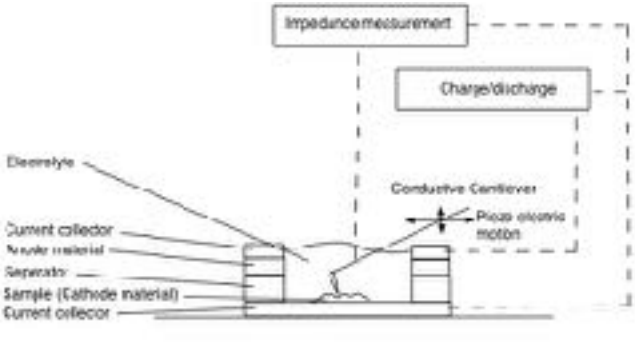


Figure 2: Operando AFM measurement inside a working Lithium Ion Battery combined with Nano impedance measurement (EIS)

Scanning Electrochemical Microscopy is another scanning probe technique that can image the reactivity of a surface at micron scale. A metal probe covered by glass, where only the top of the probe is exposed, is biased on a certain voltage, and causes redox reactions with the sample. The probe of the AFM can be isolated on a way that only the tip of the probe is insulating causing a combined measurement of AFM and SECM is possible on nanoscale. For studies on batteries these experiments with the AFM set-up needs to be carried out in an inert glovebox environment to avoid any contamination with oxygen and particularly moisture.

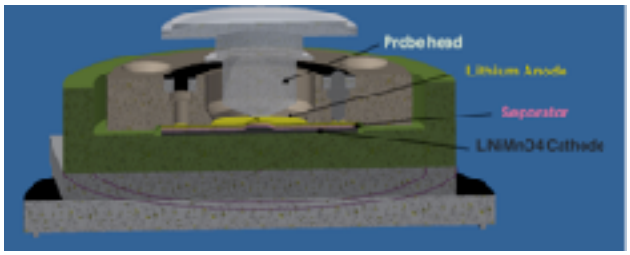


Figure 3: Temperature controlled sampleholder with integrated Lithium Ion Battery

For in-situ and operando measurements on anode-electrolyte and cathode-electrolyte interfaces and their formed interphases, a special sample holder design was developed, that allows for electrochemical measurements on the nanoscale. In Figure 2, a

cross-section drawing shows the sample holder with an integrated Li-ion cell, which is accessible for the scanning probe of the AFM. The design with electrical connections to the negative and positive electrodes makes it possible to charge and discharge the cell while running an AFM experiment. Surface scanning and approach measurements on the working electrode, here the cathode, during battery operation will provide new information about the growth of the Solid Electrolyte Interphase. The experiments can be carried out as a function of important ageing parameters, for instance temperature and charging currents. This information is of paramount importance for modelling the influence of the SEI on the ageing processes in relation to the charging circumstances.

In order to monitor the ageing as a function of temperature, the sampleholder is thus equipped with a temperature controller via a Peltier cooler/heater element. Since the counter electrode, the nano-tip, is very small, and we would like to mimic similar current densities as used in a standard Li-ion battery, we need to use a nano-ampere potentiostat to measure operando the impedance.

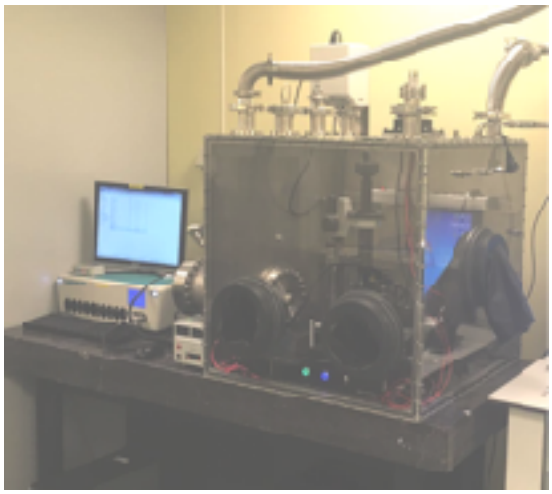


Figure 4: Atomic Force Microscope set-up for operando measurements inside a glovebox system.

A dedicated modular glovebox system is integrated with a vibration insulated stone table, and is used for performing the AFM/SECM measurements in an inert Ar gas environment, with O_2 and H_2O concentrations below 1 ppm, see figure 4. Special feedthrough connections are constructed in the side-walls of the glovebox for cables and glassfibers needed for AFM set-up and Potentiostat/Electrostat sample-connections.

2.2. Sample preparation

To define parameters with this AFM methode special requirements are set for the sample materials. Substrates needs to have a thickness of at least 0,5mm to avoid movements of the sample during AFM scanning. According to figure 1 the diameter of the active material spot needs to be smaller than the separator and the Lithium ring in order to force battery behaviour between the AFM reachable cathode material and the lithium anode. The roughness of the investigated cathode layer largely determines the possible resolution of the measurement which makes it important to have small grain sizes. The layer must be pure and homogeneous. All these requirements leads to a chosen preparation methode of samples by electrospray deposition[8].

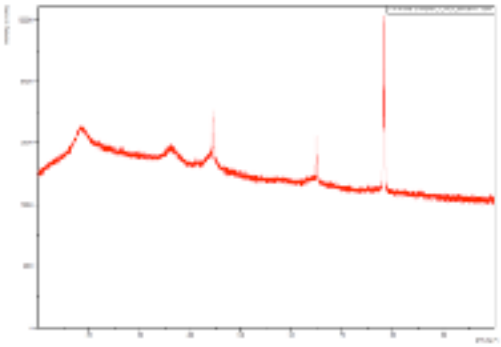


Figure 5: RD pattern of $LiNi_{0.5}Mn_{1.5}O_4$ on aluminium substrate.

For this study a thin layer of $LiNi_{0.5}Mn_{1.5}O_4$ was deposited on polished aluminium substrate by electrospray. The spray solution was prepared by carefully solving Litiumnitrate, Manganese(II) nitratetetrahydrate and Nickel(II)nitratehexahydrate in 2-propanol. The spray conditions (flowrate 0,5ml/h, potential 12,5kV, substrate temperature 450 C, substrate-needle distance 50mm) where constant during the 1800 seconds deposition.

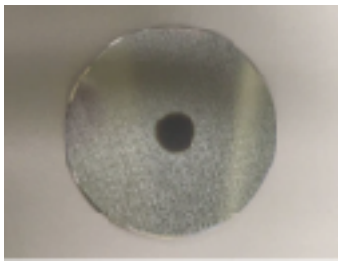


Figure 6: Sprayed $LiNi_{0.5}Mn_{1.5}O_4$ cathode on polished aluminium substrate used for operando AFM measurements.

On Figure 4 a sprayed $LiNi_{0.5}Mn_{1.5}O_4$ s with a diameter of 2 mm active material on a substrate of polished aluminium is shown.

The X-ray powder diffraction of figure 3 shows clearly that a layer with $LiNi_{0.5}Mn_{1.5}O_4$ was deposited on the substrate. Parts of this deposited layer consists of particles with grain sizes between 100 and 200 nm, which allows for AFM resolution in the same order.

2.3. Results

Here we report initial tests of the in-situ and operando AFM set-up and the electro-sprayed cathode material. The experiments where carried out using a NT MDT NTEGRA Atomic Force Microscope, situated in a costumized glovebox and stabilised for vibrations by a Halvionics i4, positioned on a stone table to avoid any vibrations. The system we selected for Nano Ampere potentiostat/galvanostat measurements is a "Autolab PGSTAT302N" with low current Amplifier module "ECD". In order to present the possibilities of the new facility, a number of different measurements have been performed. An overview of the most important results of these exploratory measurements is given below.

2.3.1. Impedance measurements

Impedance measurements with which the principle of nano scale measurements has been demonstrated have been carried out successfully. The measurements where performed with an electrically conductive AFM tip with a resonance frequency of 75 kHz and a force constant of 2,8 N/m (Nanosensors PPP-EFM). The measurement was carried out according to the principle of figure 2, with the difference that the sample only consisted of a collector (copper substrate) without cathode material. the Impedance was measured between a copper collector (polished copper plate with diameter of 7mm, electrically connected) and the electrically conductive AFM tip in a 1,0M LiPF6-EC/DMC liquid electrolyte (Sigma-Aldrich).

The AFM tip was brought to the sample surface using the normal software controlled landing procedure. When the landing was competed contact was checked by performing an Ohmic resistance test whereafter an impedance spectroscopy measurement was started. Impedance measurements where repeated at different sample-tip distances.

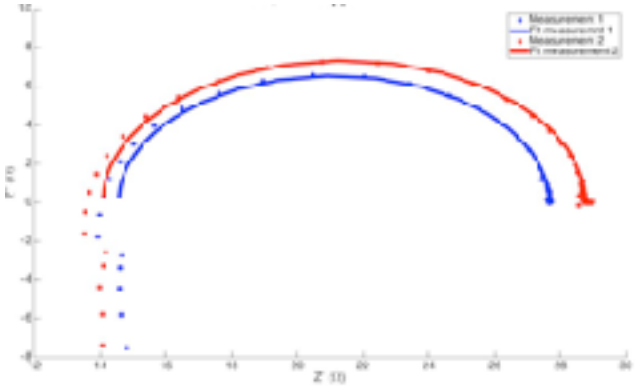


Figure 7: Impedance measurements on two different distances between copper substrate and conductive probe-tip. At measurement 1 the tip is in landed situation, measurement 2 the tip is lifted 10 nm from the surface. The data is fitted with a Randles cell.

The blue line in figure 4 gives the data for a landed tip. The Randles[9] circuit behaviour of the impedance can be explained by the weak contact caused by the low spring constant of the cantilever[9]. By moving the tip from the sample, the impedance increases. The red curve shows the impedance plot at a distance of 10nm from the surface.

2.3.2. Operando visualising of the lithium plating proces

A metallic lithium anode was added to the system of figure 1 and a current of 4 mA/cm^2 in relation to the copper surface was used to induce lithium ion transport to the copper substrate which causes lithium plating. Figure 8a shows an AFM morphologic scan of the copper surface (resolution 20nm), where the micro scratches of the polishing are clearly seen. Figure 8b shows an AFM morphologic scan 5 minutes after the potential was started. The micro scratches are covered with lithium and a difference of approximately 20 to 40 nm in height is seen on the scan. Again after 5 minutes the scan of figure 8c was taken during plating proces where the height difference is even bigger and in the order of 40 to 50 nm. Directly after this scan the measurement was stopped and the sample was taken to a Scanning Electron Microscope (SEM: Jeol JSM 7900F). Figure 8d shows the SEM picture of the plated subtsrate, which shows that lithium plating has taken place with inhomogeneous distribution on the sample surface causing deposition island spots, confirming the results of the operando AFM measurements.

2.3.2. Battery behaviour of sample holder with sprayed sample cathode

The copper substrate was replaced by a cathode as shown in figure 6. The sprayed coating of $LiNi_{0.5}Mn_{1.5}O_4$ was constructed

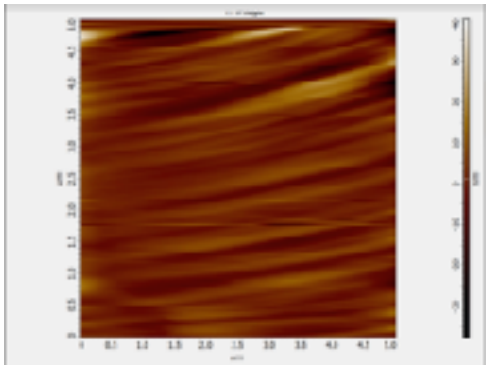


Figure 8a: Morphology scan of the copper substrate. The polish scratches are clearly visible.

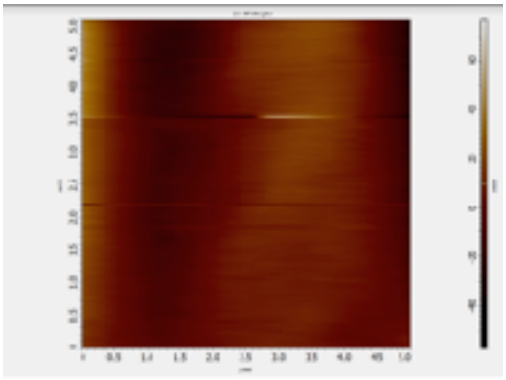


Figure 8b: Operando morphology scan of the substrate after 5 minutes of lithium plating.

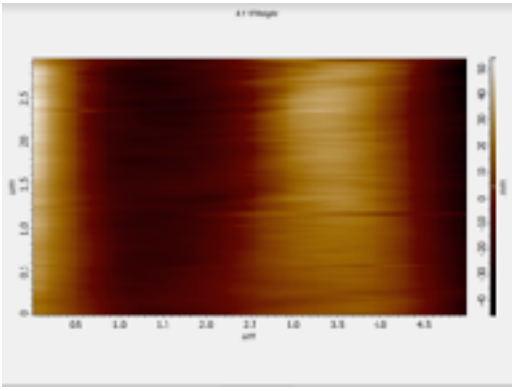


Figure 8c: Operando morphology scan of the substrate after 10 minutes of lithium plating..

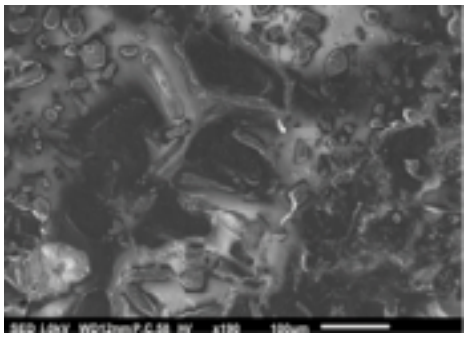
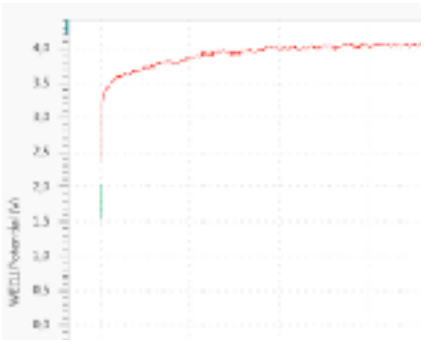


Figure 8d: SEM picture of the sample after operando plating measurements.

into the sample holder of figure 3 in such a way that a battery was created between the sample and the Lithium metal anode. A current of 0,15 mA was used to charge the substrate in the AFM accessible situation. Figure 9 shows a voltage plot of the $LiNi_{0.5}Mn_{1.5}O_4$ versus Lithium where battery behevour of the sample holder is proven.

3. CONCLUSION

This first measurements show that the technology offers good possibilities for performing in situ and operando measurements on lithium ion batteries. This article only gives the first results that are used to characterise the set-up and to test the measurements and procedures. The poster presentation will show more results in which, among others, a battery is measured



consisting of an electro spray cathode and a lithium anode. Also a model[2,3] will be used and extended with parameters to understand the processes that play a key role on the cathode and causes ageing. This measurement is currently being conducted and will be presented on the EVS31.

REFERENCES

(1) Jens groot, “State of health estimation of Li-ion batteries: ageing models”, Chalmers university of Technology, Gothenburg, Sweden, 2014

(2) Long Lam, Pavol Bauer, “Practical Capacity Fading Model for Li-Ion Battery Cells in Electric Vehicles”, 0885-8993 IEEE (2013)

(3) Long Lam, Pavol Bauer, Erik Kelder, “A practical Circuit-based Model for Li-ion Battery Cells in Electric Vehicle Applications”, 978-1-4577-1250-0 IEEE (2011)

(4) Low Wen Yao, Azis J. A. , Pui Jee Kong, N. R. N. Idris, “A practical Circuit based Model for Li-ion Battery Cells in Electric Vehicle Applications”, IEEE, 2013, 978-1-4799-0224-8

(5) Dervis Emre Demirocak, Bharat Bhushan, “In situ atomic force microscopy analysis of morphology and particle size changes in Lithium Iron Phosphate cathode during discharge”, Journal of Colloid and Interface Science 423 (2014) 151-157

(6) P.P.R.M.L. Harks, F.M. Mulder, P.H.L. Notten, “In situ methods for Li-ion battery research: A review of recent developments”, Journal of Power Sources 288 (2015) 92-95

(7) Low Wen Yao, Aziz, J.A., Pui Yee Kong, N.R.N. Idris, “Modeling of Lithium Ion Battery Using MATLAB/Simulink”, 978-1-4799-0224-8/13 IEEE (2013)

(8) M. Valvo, E. Garcia-Tamayo, U. Lafont, E.M. Kelder, “Direct synthesis and coating of advanced nanocompostite negative electrodes for Li-ion batteries via electrospraying”, Journal of power Sources 196 (2011) 10191-10200

(9) Ryan O’Hayre, Minhwan Lee, Fritz B. Prinz, “Ionic and electronic impedance imaging using atomic force microscopy”, Journal of applied physics volume 95 Number 12