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METALLOGRAPHIC PREPARATION OF LITHIUM-ION BATTERIES

A COMPLETE METALLOGRAPHIC PREPARATION FOR PERFORMING QUALITY CONTROL ON DIFFERENT PARTS OF A LIB

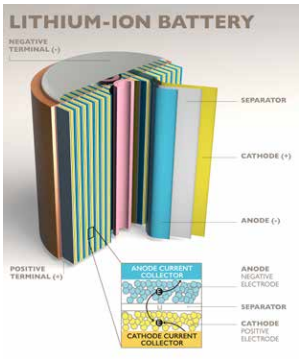

Figure 1: The structure of a conventional LIB.

Introduction

Li-based battery technologies have evolved significantly over the past three decades, starting with the early Li-metal anodes, and continuing to commercial Li-ion batteries today. The story of Li-based batteries is rich with breakouts and historical developments [1]. The history of lithium-ion batteries began in 1962. The very first batteries could not be recharged after a single discharge (primary battery). The material of the negative electrode was lithium, and the material of the positive electrode was manganese dioxide. This battery was introduced in 1972 by the company Sanyo on the market. In 1985, the company Moli Energy developed the first rechargeable battery (secondary battery) based on lithium (negative electrode) and molybdenum sulfide (positive electrode). This design, however, had safety problems due to the lithium on the negative electrode. The next step towards lithium-ion batteries was achieved by coating on both sides of the electrodes, which allowed lithium to be stored and removed and had a high voltage potential. The Sony company developed the first rechargeable lithium-ion battery and launched it in 1991. The active material of the negative electrode was carbon, and that of the positive electrode was lithium cobalt dioxide [2].

From the beginning one of the most challenging procedures was to choose the best compounds for electrodes and specially for the cathode. The requirements of high cycle stability and acceptable specific capacity limit the choices of electrode materials to a few. Using aluminum foil coated with metal oxide particles in the cathode and copper foil coated with graphite in the anode is one of the most common combinations. Figure 1 shows the structure of a conventional LIB. The foils can be coated on one or both sides.

Various Lithium-Metal-Oxide compounds are used in the cathodes. Layered oxides like Li(Ni1/3Co1/3Mn1/3)O2, for example, can obtain high specific capacity. Due to the lower price of Mn-rich compounds compared to Ni/Co-rich compounds, they are more favorable for manufacturers [3]. The most important candidates for anode and cathode materials can be seen in figures 7 and 11 respectively.

One of the procedures for the quality control of LIBs is metallographic investigation of the cap and case of the battery, the spot welding or the electrodes. Since these parts are made of different materials, they require different preparation methods. In the following paragraphs the various preparation methods as well as the target of each preparation will be discussed.

Metallographic preparation of cap and casing of the battery

The battery casing as the location of the active and passive components of a battery system plays a decisive role for the functionality, safety, and service life of the energy storage system. It protects the components, some of which are sensitive, from harmful environmental influences such as water, moisture, or dust, and is thus crucial for safe and reliable operation in the long term. Since car batteries are normally located outside the vehicle cabin, usually in the floor area, the housing is exposed to extreme environmental influences such as temperature, humidity, splash water, salt spray, dust, or stone chips. Therefore, high mechanical stability and corrosion resistance are crucial, even under rough external conditions [2].

One of the QC procedures for the casing of the batteries is metallographic preparation and investigation under optical as well as scanning electron microscope. The cap of the batteries can be cut with rotational clamping tool on Qcut 200 A. Figure 2 shows how the sample can be clamped in the machine to cut the cap and take the jelly roll out.

The preparation method for the casing and the cap of the LIB can be seen in table 1. In most of the cases the cap of the batteries is made of ferritic steel with nickel-base coating. Here, appropriate preparation can remove artefacts such as edge rounding, damage the coating by using the wrong forces and orientations, smearing of the base material as well as nickel coating and many other possible artefacts. The preparation method in table 1 is a preparation method developed by QATM with its specific machines and consumables, which assure the most accurate results after preparation.

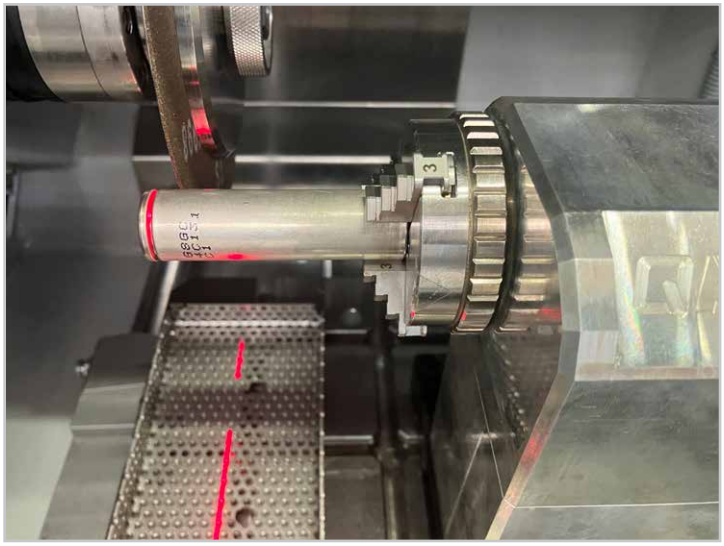

Figure 2: How to clamp the LIB in rotational clamping tool to cut the cap and take the jelly roll out.

Table 1. The developed parameters for grinding and polishing the cap and the casing of LIBs

EQUIPMENT	SAMPLE HOLDER	PRESSURE MODE				
Qpol 300 A1 ECO+		Individual				
STEP	**MEDIUM**		**rpm**		**Single Pressure N**	**min**
Planar grinding	VEGA 54 µm	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	Till flat surface (≈1:00)
Pre-polishing	BETA	Dia suspension Poly, 9 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	►► Counter Rotation	25	5:00
Polishing	SIGMA	Dia suspension Poly, 3 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	►► Synchronous Rotation	25	4:00
Final polishing	OMEGA	Eposil F 0.1 µm	SH: 80 WP: 100	►► Counter Rotation	30	1:30 (H_2O during final 0:30)
Etching	Klemm I 3% alcoholic nitric acid					40 s 5 s
Notes	SH: The rotational speed of the sample holder WP: The rotational speed of the working plate Pre-dosing time for diamond suspension 9 µm and 3 µm and lubricant: 3 s The dosing interval for dia. suspension 3 µm and 1 µm: each 30 s for 1.5 s The dosing interval for lubricant 3 µm and 1µm polishing: each 60 s for 1.5 s					

Figures 3 and 4 show the microstructure of the cap of a LIB. As can be seen in Figure 2, the cap is made of coated ferritic steel. For these samples, the use of the right parameters as well as appropriate consumables is crucial, because using the wrong forces or consumables can round the edge and affect the measurement results.

Figure 3. The microstructure of the cap of a LIB after etching with 3% alcoholic nitric acid. To measure the grain size of the cap, color etching with Klemm I can be carried out. The result after etching with Klemm I can be seen in Figure 4.

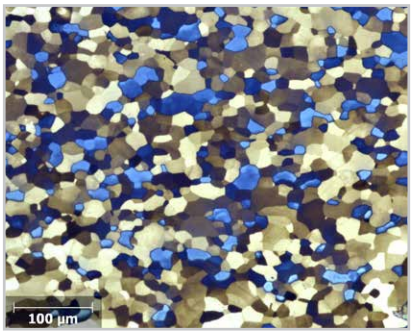

Figure 3 (left): The microstructure of the cap of a LIB after etching with 3% alcoholic nitric acid.
Figure 4 (right): The microstructure of the cap of a LIB after etching with Klemm I.

Figure 5 shows the back scattered electron image from the cap under SEM. Also, the chemical composition of the coating can be measured under EDS-detector in a scanning electron microscope (SEM). Figure 6 shows the coating-thickness measurement which was performed by “QPIX Control 2” software.

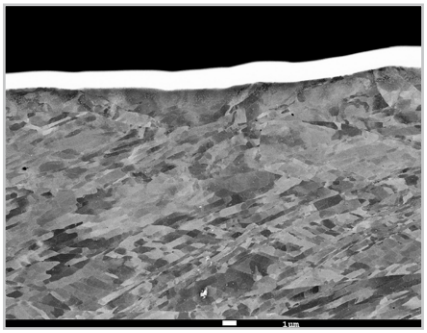

Figure 5. The BSE image of the cap, the coating can be clearly seen on the top.

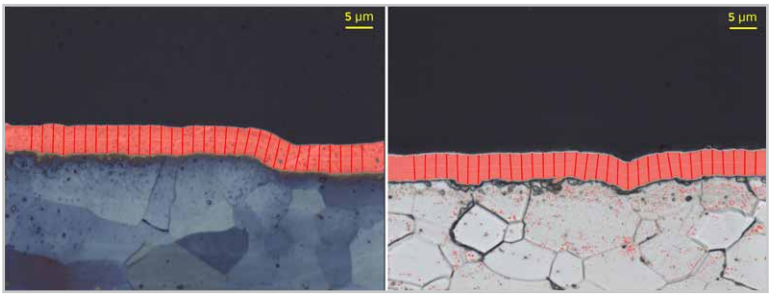

Figure 6. Thickness measurement by QPIX control 2. The final thickness is 5.1 µm.

Further quality control that can be done on the cap and casing of the LIBs is hardness testing. In this example, QATM’s Qness 60 A+ Evo hardness tester has been used to perform hardness testing HV1. Figure 7 shows the results as well as the place of the indentations.

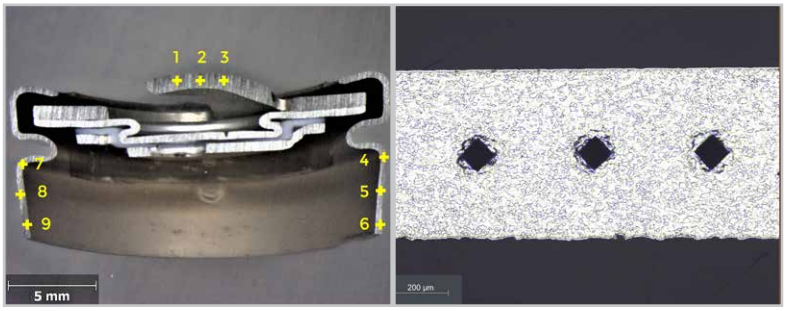

Figure 7. The HV1 hardness test on the cap and the casing of LIB. Hardness of the cap: 117.3 HV / Hardness of the casing: 210.6 HV.

Metallographic preparation of anode foils

Figure 8 shows the possible anode materials. Nowadays, the conventional anode consists of a copper foil as current collector, coated with graphite on one or both sides. Here, the challenge is to prepare the samples without damaging the foil or coating and without causing smearing effects. Smearing lets the thickness of the copper foil appear greater than it actually is under the microscope and can thus lead to incorrect decisions. In addition, the graphite layer can detach from the coating due to incorrect metallographic preparation.

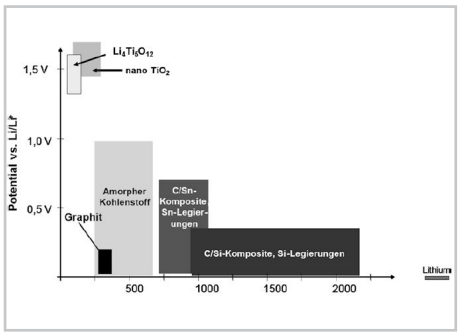

Figure 8. Specific storage capacity and potential versus Li/Li+ of the main anode materials.

The best way to mount the anode or cathode foils is to use Epoxy-resin-base mounting materials. KEM 92 is a mounting material from QATM with epoxy resin. The slow chemical reaction between the resin and the hardener in this cold mounting material assure the lowest gap between the samples and the mounting material. By using cold mounting accessories, several foils can be mounted in one sample. The preparation method in table 2 was developed by QATM with its specific machines and consumables, which assure the most accurate results after preparation of anode foils.

Table 2. The developed parameters for grinding and polishing of LIBs-anode foils.

EQUIPMENT	SAMPLE HOLDER	PRESSURE MODE				
Qpol 300 A1 ECO+		Individual				
STEP	**MEDIUM**		**rpm**		**Single Pressure N**	**min**
Planar grinding	SiC paper P600 + Quick-Tap	H_2O	SH: 120 WP: 200	▶▶ Synchronous Rotation	25	Till flat surface (≈1:00)
Planar grinding	SiC paper P1200 + Quick-Tap	H_2O	SH: 120 WP: 200	▶▶ Synchronous Rotation	25	0:45
Planar grinding	SiC paper P2500 + Quick-Tap	H_2O	SH: 120 WP: 200	▶▶ Synchronous Rotation	25	0:45
Planar grinding	SiC paper P4000 + Quick-Tap	H_2O	SH: 120 WP: 200	▶▶ Synchronous Rotation	25	0:45
Polishing	SIGMA	Dia suspension Poly, 3 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	▶▶ Synchronous Rotation	25	5:00
Final polishing	SIGMA	Dia suspension Poly, 1 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	▶▶ Synchronous Rotation	25	5:00
Notes	SH: The rotational speed of the sample holder WP: The rotational speed of the working plate Pre-dosing time for diamond suspension 3 µm and 1 µm and lubricant: 3 s The dosing interval for dia. suspension 3 µm and 1 µm: each 30 s for 1.5 s The dosing interval for lubricant: each 60 s for 1.5 s					

Figures 9 and 10 show the structure of anode foil under optical microscope. The connection between coating and foil, the straightness of the copper foil and possible manufacturing defects can be interesting issues in metallographic analyses of LIB-anode foils. Figure 11 shows the result from an EDX-detector, here the contained elements can be determined.

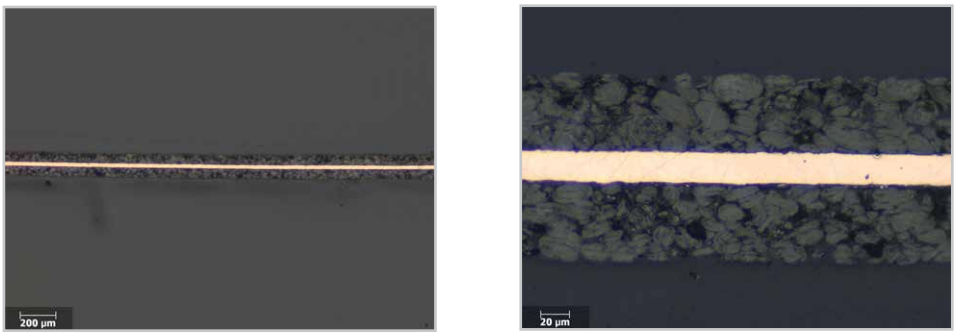

Figure 9. The structure of anode with low magnification. Here the straightness of the copper foil can be investigated.
Figure 10. Figure 8 with higher magnification.

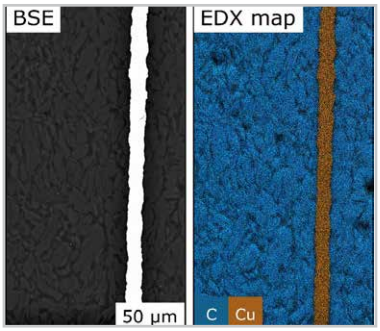

Figure 11: The result of the analysis with the EDX detector. As can be seen, Cu element is determined with orange color and graphite (carbon element) with blue color.

Metallographic preparation of cathode foils

One of the most popular combinations for the cathode material is to use an aluminum foil as a current collector, coated on one or both sides with metal oxides particles such as LiNiMnCo oxides. Figure 12 shows various cathode materials with their properties. The preparation method in table 3 is a preparation method developed by QATM with its specific machines and consumables, which assure the most accurate results after preparation of cathode foils.

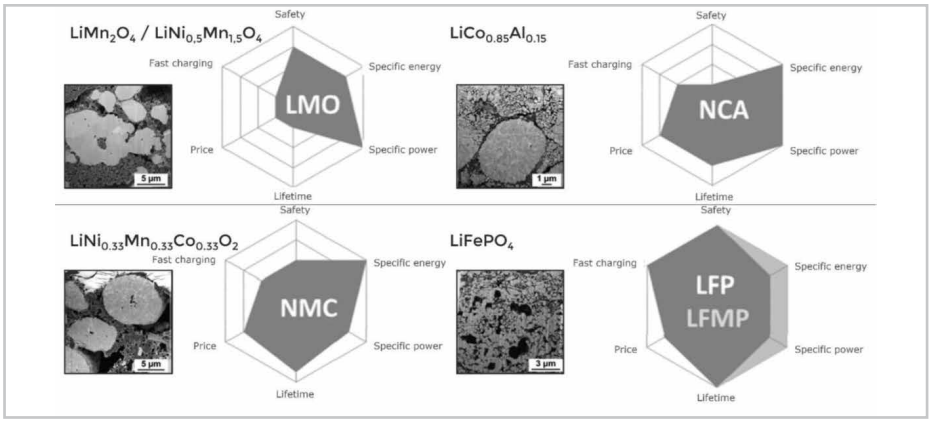

Figure 12: Comparison and FIB cut on different active materials for cathode coating [2,4].

Table 3. The developed parameters for grinding and polishing of LIBs-cathode foils.

EQUIPMENT	SAMPLE HOLDER	PRESSURE MODE				
Qpol 300 A1 ECO+		Individual				
STEP	**MEDIUM**		**rpm**		**Single Pressure N**	**min**
Planar grinding	SiC paper P600 + Quick-Tap	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	Till flat surface (≈1:00)
Planar grinding	SiC paper P800 + Quick-Tap	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	0:45
Planar grinding	SiC paper P1200 + Quick-Tap	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	0:45
Polishing	GAMMA	Dia suspension Poly, 3 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	►► Synchronous Rotation	25	25:00
Polishing	GAMMA	Dia suspension Poly, 1 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	►► Synchronous Rotation	28	40:00
Final polishing	OMEGA	Eposil F 0.1 µm	SH: 75 WP: 90	►► Counter Rotation	20	30:00 (last 1:00 minute just with water)
Notes	SH: The rotational speed of the sample holder WP: The rotational speed of the working plate Pre-dosing time for diamond suspension 3 µm and 1 µm and lubricant: 3 s The dosing interval for dia. suspension 3 µm and 1 µm: each 30 s for 1.5 s The dosing interval for lubricant: each 60 s for 1.5 s Pre-dosing time for Eposil F 0.1 µm: 5 s The dosing interval and length for Eposil F 0.1 µm: each 60 s for 2 s					

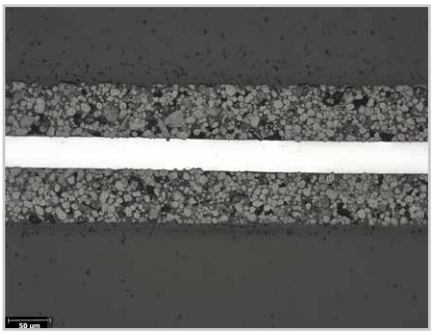

Figure 13: Aluminum foil coated on both sides with metal-oxide particles.
Figure 14: Figure 13 with higher magnification.

Here also the EDX-detector can be used to determine the contained elements of the current collector as well as coating. Figure 15 shows the results after EDX analyses.

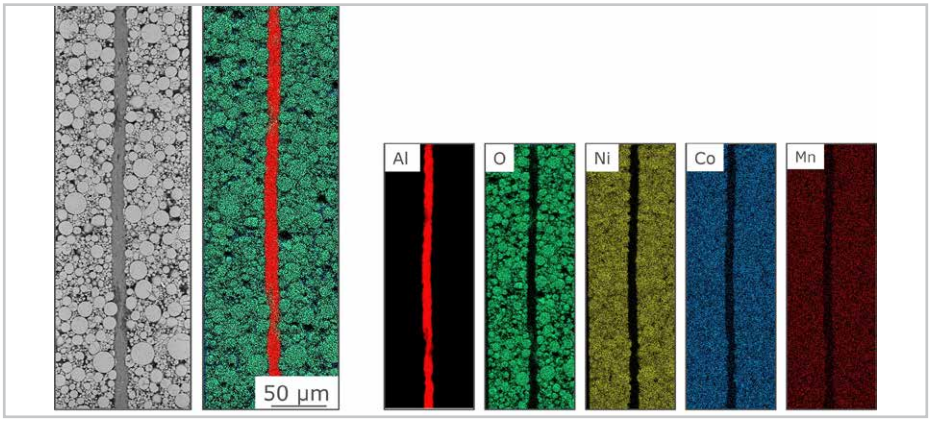

Figure 15: The EDX results for the cathode foil.

Metallographic preparation of resistance spot welding

Last but not least is metallographic preparation of spot weld on the cap of the battery. This investigation is vital for the aerospace industry. The space flight environment is especially sensitive to risks, particularly when it involves potential for fire within the habitable volume of the International Space Station (ISS). In larger battery packs such as Robonaut 2 (R2), numerous Li-ion cells are placed in parallel-series configurations to obtain the required stack voltage and desired run-time or to meet specific power. Investigation of the spot weld of these LIBs is essential to ensure safety in the ISS. Here, the most important issue is not to cover the pores due to incorrect metallographic preparation, because with the wrong parameters the material can smear and close the surface of the pores.
Table 4 lists the appropriate parameters for preparation of these spot welds and figure 16 shows some measurements on these spot welds [5].

Table 4. The developed parameters for grinding and polishing of resistance spot welds on the LIBs.

EQUIPMENT	SAMPLE HOLDER	PRESSURE MODE				
Qpol 300 A1 ECO+		Individual				
STEP	**MEDIUM**		**rpm**		**Single Pressure N**	**min**
Planar grinding	SiC paper P320 + Quick-Tap	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	Till flat surface (≈1:00)
Planar grinding	SiC paper P600 + Quick-Tap	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	0:45
Planar grinding	SiC paper P1200 + Quick-Tap	H_2O	SH: 120 WP: 200	►► Synchronous Rotation	25	0:45
Polishing	SIGMA	Dia suspension Poly, 3 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	►► Synchronous Rotation	25	5:00
Polishing	ZETA	Dia suspension Poly, 1 µm + Lubricant (alcohol-base)	SH: 120 WP: 150	►► Synchronous Rotation	25	2:00
Notes	SH: The rotational speed of the sample holder WP: The rotational speed of the working plate Pre-dosing time for diamond suspension 3 µm and 1 µm and lubricant: 3 s The dosing interval for dia. suspension 3 µm and 1 µm: each 30 s for 1.5 s The dosing interval and length for lubricant: each 60 s for 1.5 s					

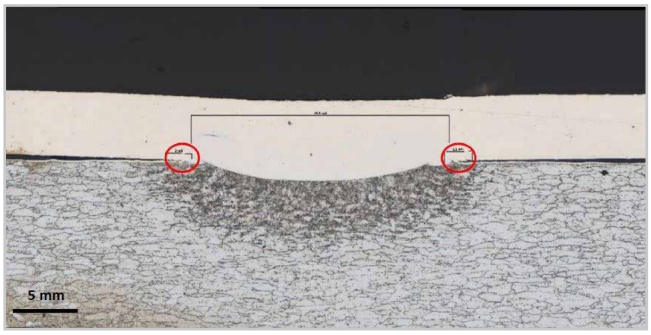

Figure 16: The spot welds on the cap of the battery. The red circles show tiny cracks on both ends of the spot weld. 3 % alcoholic nitric acid has been used as etchant [5].

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