Technical White Paper

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Using Attension Tensiometers to Evaluate Wettability in Li-ion Batteries

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[Progress Together]

Improving Li-ion battery performance and safety through wettability measurements

Lithium-ion batteries are the main energy storage technology for mobile devices such as smartphones and laptops. A recent increase in demand for plug-in-hybrids and electric cars has initiated the discussion of whether Li-ion battery technology will ever be good enough for mass-market full electrification.

Wettability has been recognized as one of the key factors affecting both the performance of the Li-ion batteries as well as manufacturing cost. The wettability of materials is commonly studied with either optical or force tensiometers. Both have been applied to study the wetting of materials used in Li-ion batteries.

Li-ion batteries have several interfaces where wettability plays a role

There are multiple different interfaces in Li-ion batteries where the liquid and the solid are in contact. All of these interfaces play a role in the battery performance.

Lithium-ion battery is composed of porous positive and negative electrodes which are filled with electrolyte solution and separated by a separator. The negative anode side consists of a current collector which is copper and electrode slurry which is a complex mixture of active material (graphite), solvent, binder, and additives. Several solid-liquid interfaces can be recognized. In electrode slurry, the graphite particles are in contact with the liquid phase. The current collector (copper) is coated with the slurry and the interface between the copper and the slurry is formed. The positive cathode side has typically Lithium metal oxide particles in the slurry and the slurry is in contact with the aluminum which acts as a current collector. A separator is a physical barrier between the anode and the cathode. All of the components, anode, cathode, and separator are in contact with the electrolyte which is commonly lithium salt in an organic solvent.

While the cathode and anode determine the performance of the battery, the electrolyte, and the separator are responsible for the safety of the battery.

Good wettability between the materials is required for the optimum operation of the Li-ion batteries.

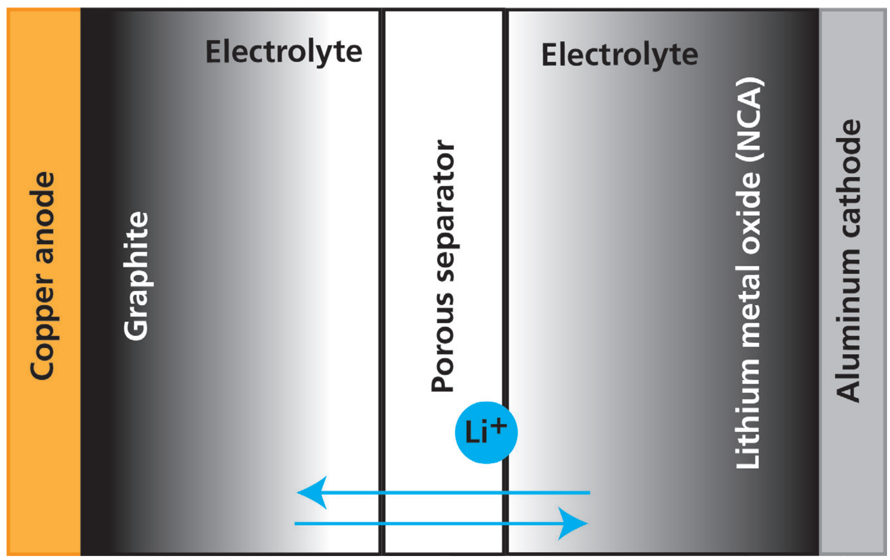

Figure 1. Several solid-liquid interfaces can be found in Li-ion battery

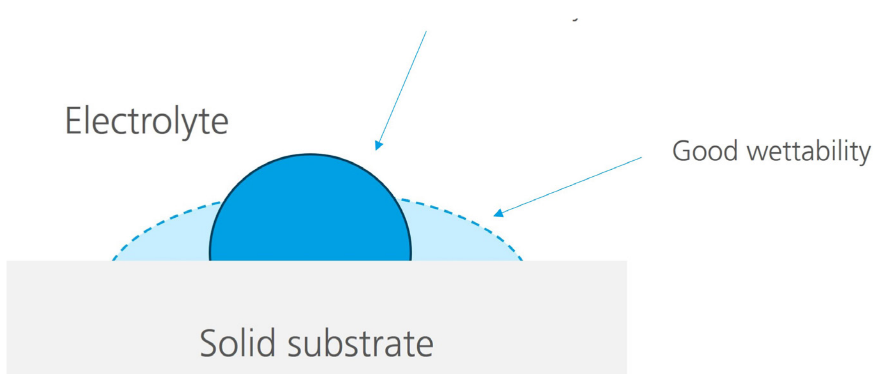

Figure 2. Good wettability betweent the solid and the liquid is required for optimum performance and safety

Tensiometer measurements to study the materials in Li-ion batteries

To study the wettability between solid and liquid, optical and force tensiometers are commonly used. With tensiometers, it is possible to measure the surface tension of a liquid as well as study the interaction between a solid and a liquid.

Optimize electrode slurries with surface tension and Washburn measurements

The electrode slurry is a complex mixture of active material, conductive additive, polymer binder, and solvent. Wetting of the active material particles in the slurry is crucial as poor wettability leads to uneven dispersion of the particles.

The surface tension of the slurry affects the wetting ability of the current collector. Too high surface tension will lead to uneven spreading of the slurry as well as higher film thickness.

Case Study: Effect of surface treatment time on wettability of carbon powder

To study the effect of surface treatment time on the wettability of carbon powder, a force tensiometer with the Washburn method is utilized. The measurement is done by packing the carbon powder into a container with holes in the bottom. Filter paper is used to prevent powder from escaping the containers. The container is hung on a sensitive balance and lowered into the liquid so that the very bottom of the container is immersed in the liquid (see figure 6.for reference) The mass uptake as a function of time is recorded by the balance. To determine the contact angle, the measurement is first done against a completely wetting liquid such as n-heptane and then against the liquid of interest, in this case, water [1].

Sample: Carbon powder with different levels of surface treatment.

Method: Washburn method to determine the water contact angle of the carbon after different surface treatment times

The measurements show (figure 3.) a clear decrease in water contact angle as a function of surface treatment time.

Coating of the current collector

Electrode slurry is coated on the current collector which is either copper (anode) or aluminum (cathode). The proper spreading and adhesion of the slurry on the current collector is crucial for the optimum performance of the Li-ion batteries. The contact angle between the slurry and the current collector can be measured with either the sessile drop method with an optical tensiometer or the Wilhelmy plate method with a force tensiometer.

Calendering

Calendering is a common compaction process for lithium-ion battery electrodes. The purpose of calendering is to reduce the porosity of the electrode which improves the particle contact and thus enhances the energy density of the battery. Calendering will significantly impact the pore structure and thus also the wettability of the electrode [1]. Calendering also affects the surface texture of the electrode which needs to be considered when the wettability of the electrode is evaluated. The effect of calendering on electrode wettability has been studied by determining the wetting rate with the force tensiometer [2]. The measurement is based on the so-called Washburn method [3] where the porous sample is immersed into the liquid and a highly sensitive balance is used to record the mass uptake as a function of time. Optical tensiometer offers another tool to study the wettability of the electrodes.

Case study: Contact angle measurement on uncompressed and compressed electrodes

To study the effect of calendering on wettability, the contact angles with Attension Theta Flow optical tensiometer were measured.

Solid sample: Lithium Nickel-Cobalt-Aluminum Oxide (NCA) coated on aluminum foil (Uncompressed and compressed)

Liquid: Dimethyl carbonate solvent (DMC)

The measurements clearly show (figure 4) that calendering increases the contact angle of dimethyl carbonate solvent on the electrode. This indicates that the wettability of the electrode is decreased with calendering which can cause issues in the subsequent filling of the electrolyte.

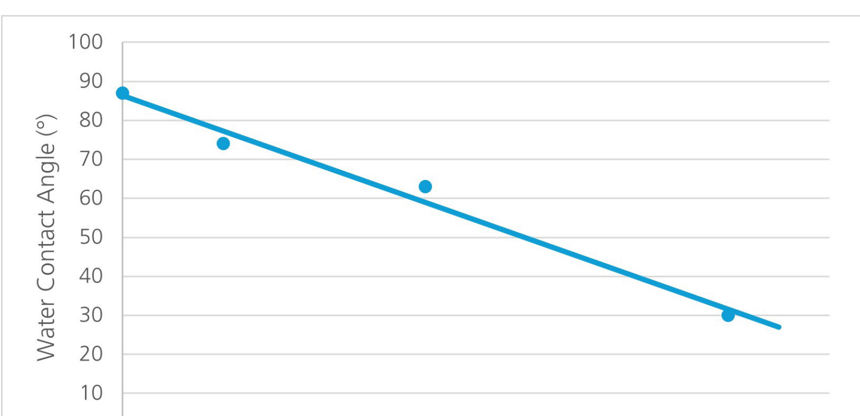

Figure 3. Water contact angle of carbon powder as a function of surface treatment time

Separator wettability

A separator is a key component of the battery as it is placed between positive and negative electrodes. It prevents the battery short circuit by blocking the physical contact between the two electrodes but at the same time allows the flow of lithium-ion. A separator has been considered as an inactive component of the battery, but its properties are of utmost importance for the performance and safety of the batteries.

A separator is a porous membrane between electrodes of opposite polarity. A variety of different separator materials have been used over the years but today's commercial separators are commonly made of polyolefins, such as polyethylene or polypropylene.

The wettability by electrolyte is a critical characteristic of lithium-ion battery separator as electrolyte adsorption is essential for ionic transport. Polymeric separator materials are inherently hydrophobic with insufficient wettability to conventional organic electrolytes. Different approaches have been considered to increase the wettability of the separator material. These include different types of coatings using for example electrospinning [1] or atomic layer deposition (ALD) [2] and fabrication of composite separators [3].

Case study: Wettability of polymeric and ceramic separators

To study the effect of separator material on wettability, contact angles with Attension Theta Flow optical tensiometer were measured.

Solid sample: Polymer and ceramic separator

Liquid: Dimethyl carbonate solvent (DMC)

The measurements show that the wettability of the ceramic separator is slightly better than that of the polymer separator indicating better performance of the ceramic one.

	CA of uncompressed electrodes (°)			CA of compressed electrodes (°)		
	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
Measurement 1	17.2	16.1	18.5	34.1	26.9	32.0
Measurement 2	16.2	16.6	14.2	31.6	24.8	32.3
Measurement 3	14.5	13.3	14.4	32.2	28.5	29.5
Average	**16.0**	**15.3**	**15.7**	**32.7**	**26.8**	**31.3**
Standard deviation	**1.14**	**1.43**	**1.97**	**1.05**	**1.51**	**1.29**

Figure 4. Contact angle of DCM on uncopmressed and compressed electrodes

Speed up electrolyte filling

The wettability of the electrode material with the electrolyte solution is one of the challenges in the development of high-performance lithium-ion batteries.

Transferring from small-sized batteries into large-scale applications for electric vehicles poses significant challenges to battery manufacturing. One of the key steps in manufacturing is the addition of the electrolyte solution into a porous electrode by a precision pump. In this step, the electrolyte should permeate and fill the pores of the electrode. This process is called a wetting process and can take several days at elevated temperatures because of the poor wettability of the electrode, long diffusion distances, and hindered diffusion as gases are trapped within pores. The long process will increase the manufacturing time and at the same time the costs of manufacturing.

Electrolyte uptake can be measured with the force tensiometer similarly to the measurement described for electrode slurry optimization (figure 6.). In the case of electrolyte uptake measurement, an electrode material is immersed into the electrolyte solution. The electrode material is a sheet of an electrode cut into a rectangular shape that can be easily attached to the balance hook. The electrolyte is placed

	Separator materials	
	Polymer separator	Ceramic separator
Measurement 1	29.0	24.9
Measurement 2	28.6	25.3
Measurement 3	28.7	24.7
Average	**28.8**	**25.0**
Standard deviation	**0.21**	**0.31**

Figure 5. Contact angle of DCM on polymer and ceramic separator

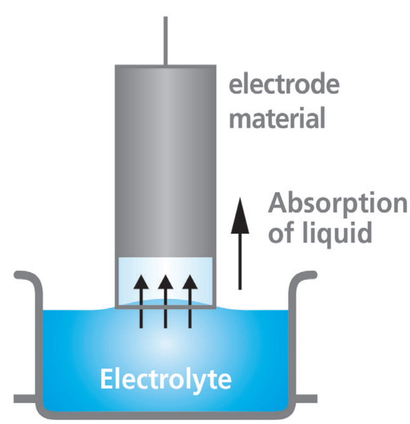

Figure 6. Schematics of the adsorption measurement for both active material contact angle measurements as well as for electrolyte uptake measurement.

in the sample container and the electrode is brought into contact. The mass uptake as a function of time is measured.

Conclusions

Wettability measurements are key to ensure optimum performance, manufacturing and safety of the Li-ion batteries. Attension optical and force tensiometers provide versitily tools for measurements needed in Li-ion battery research and develoment..

Key opportunites tensiometers can provide

Surface tension of electrode slurry to optimize coating and drying processes

Use an optical or force tensiometer to measure the surface tension of the slurry. Lower surface tension leads to better surface wetting.

Wettability of the electrode material to maximize adhesion between the electrode and the slurry

Use an optical tensiometer to measure the contact angle between the electrode material and the slurry. Lower contact angles indicate better wettability and thus better adhesion.

Effect of calendering on electrode wettability

Use an optical tensiometer to measure the contact angle of uncompressed and compressed electrodes with electrolyte.

Evaluate electrolyte uptake to speed up the filling process

Use a force tensiometer to monitor the electrolyte uptake into electrode material.

Interested to learn more?

If you would like to learn more about Attension tensiometers and how they can help ypu in your work, please reach out and we will tell you more. We would love to hear from you.

References and further reading

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About us

At Biolin Scientific we are committed to empower professionals in Surface and Interface science and engineering to reach outstanding results faster and easier. Our instruments and sensors are tailored for advanced analysis of thin film properties and surface and interface phenomena at the nanoscale. Trusted by top universities and industrial labs worldwide, our premium solutions help solve complex challenges and drive progress in scientific research and product development. We firmly believe that brilliant minds deserve state-of-the-art instruments and expert support. Let's progress together.

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