Low Temperature Viscosity Measurements - Lovis for Battery Electrolytes

Relevant for: battery industry, electrochemical research, automotive industry

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Perform viscosity measurements down to -20 °C with Lovis 2000 M/ME with cooling option. Test even highly corrosive solvents for ion salts by using unbreakable PCTFE capillaries with small filling volumes (110 µL or 450 µL). Handling of the sample inside a glove box filled with inert gas and a hermetically closed system prevent contamination or evaporation of the sample.

1 Introduction

Since the introduction of the lithium-ion batteries in 1990, the interest in this technology has emerged steadily, not only for portable devices but also for the automotive industry. Their high energy density as well as outstanding cycle stability are the main reasons for commercial success, but several problems arise with the usage of the most common non-aqueous electrolytes, which contain lithiumhexafluoro-phosphate ($LiPF_6$) as conductive salt and a mixture of cyclic and non-cyclic organic carbonates.

In addition to the high purity required of all used solvents (e.g. traces of protic impurities such as water can cause severe deterioration of the cell performance after a short life / cycle time) the cell performance has to be stable over a broad temperature range from arctic to tropical conditions without any significant degradation. Therefore, an exact characterization of newly developed electrolytes at different temperatures is an essential part in the lithium-ion cell research today.

These challenges have to be considered for every other upcoming battery systems like magnesium ion cells or sulfur cells, too.

Therefore, research companies use different standard electrochemical measurements for monitoring batteries. In this connection viscosity, conductivity and – if required – density measurements of the electrolytes support those investigations.

The performance of the charge and discharge rate of a rechargeable battery, that is the ion transport, is characterized by the ion conductivity, which depends on the viscosity and the dielectric constant.

The viscosity of the solvent, in which the ion salt is solved, affects the mobility of ions, as shown in the Stokes-Einstein equation; mobility is inversely proportional to the viscosity:

$$mobility = \frac{1}{6\pi\eta r}$$

r ... radius of the solvated ion

Based on those viscosity measurements important conclusions on the wettability of the electrode /electro-lyte interface can be drawn, too. Fast, accurate and reproducible viscosity measurement over a wide temperature range is highly desirable for successful development of new electrolyte systems.

This application report shows how the Lovis can be used for electrolyte measurements even at tempera-tures below zero. The Lovis, equipped with cooling option and in combination with the capillary made of PCTFE, enables measurement of highly corrosive substances over a wide temperature range.

2 Instrumentation

2.1 Lovis 2000 M/ME Microviscometer with Cooling Option

Figure 1: Lovis 2000 M with cooling option

The Lovis 2000 M/ME Microviscometer measures the rolling time of a ball inside an inclined capillary. Variable inclination angles allow for measurements at different shear rates. Temperature control via Peltier elements is extremely fast and provides utmost accuracy.

For measuring at temperatures below zero, the Lovis ME Module can be equipped with a low temperature option. In combination with a recirculating cooler, it is possible to measure at temperatures as low as -20 °C (lower temperatures down to -30 °C on request, depending on the cooling liquid of the recirculating cooling, ambient temperature and ambient air humidity).

The integrated software calculates the kinematic or dynamic viscosity, provided the sample's density value is known.

2.2 PCTFE Capillaries

Figure 2: Lovis PCTFE capillaries

With the PCTFE capillaries it is possible to measure nearly every liquid, also corrosive, aggressive or hazardous solvents and electrolytes.

The measuring viscosity of a PCTFE capillary ranges from 0.8 mPa.s to 160 mPa.s.

Used material:

- Capillary: PCTFE short (110 µL)
- Capillary diameter: 1.62mm
- Ball material: Steel
- Ball diameter: 1.5 mm

2.3 Additional Equipment

- Glove box filled with argon.
- Circulation cooler plus insulated hoses. How to set up the cooling is precisely described in the documentation of Lovis 2000 M/ME.

3 Measurement

All determinations were performed manually without autosampler. The viscosity measurements were performed in a temperature range from -20 °C to +60 °C with steps of 5 °C or 10 °. For temperature table scans (TTS) two density values at two different reference temperatures were typed in manually in the "Quick Settings" ("Lovis Density TS/TTS") for every sample. The instrument automatically extrapolated the missing temperature / density values by linear extrapolation. The density values for the manual input were determined with the SVM™.

Every scan was performed twice in order to obtain a repeat determination. To check the reproducibility, all measurements were performed with Lovis and SVM™ in parallel.

3.1 Samples

- Different mixtures of organic carbonates, which contain lithiumhexafluorophosphate as conductive salt – for lithium ion batteries (LIB), either commercial available standard electrolytes or newly developed electrolyte solutions.
- Solvents containing a polar organic solvent and dioxolane added with Li-sulfur-compounds as conductive salts – for future Li-S-cell systems (LiS).
- Solvents containing a polar organic solvent plus Mg-compounds as conductive salts – for prospective Mg-ion batteries.

3.2 Instrument Settings

Measuring Method: Temperature Table Scan (TTS)
Measuring Settings:

- Temperature: scan between -20 °C to +60 °C
- Equilibration Time: no
- Measurement Cycles: 3
- Measuring Angle: Auto Angle *
- Variation Coefficient:
  0.4 % for standard electrolytes
- Measuring Distance: Short

** Adjustment was performed over an angle range from of 20° to 70° in 10° steps*

3.3 Filling of the Capillary

All samples were manually filled in an argon glove box under inert conditions. For each measurement a new steel ball was used to avoid any cross contamination from one measurement to the other. After closing the capillary with the appropriate plug, the hermetically sealed capillary was removed from the glove box.

3.4 Cleaning

The capillary was cleaned thoroughly with small brushes after every test sequence. Ethanol, deionized water and other appropriate solvents were used as cleaning liquids. If necessary, the capillary was placed into an ultrasonic bath (approximately 10 to 20 min, 30 °C, water plus standard detergent). Afterwards the capillary was dried under a pressure-less nitrogen stream.

4 Results

4.1 Comparison of Lovis and SVM™

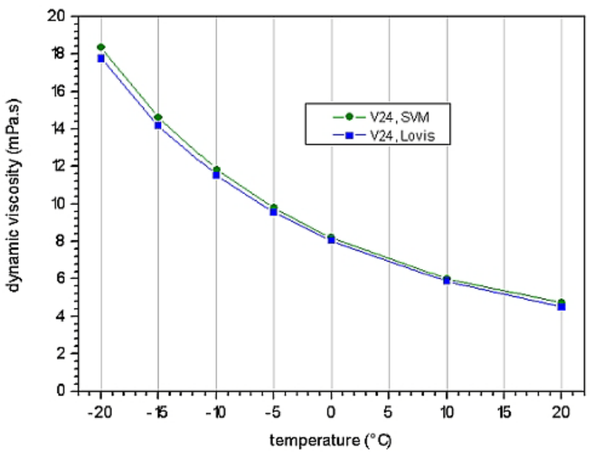

Figure 3: Reproducibility check; standard Li-ion electrolyte V24 measured with Lovis and SVM™ from +20 °C to -20 °C

4.2 Comparing Li-ion Standard Electrolytes

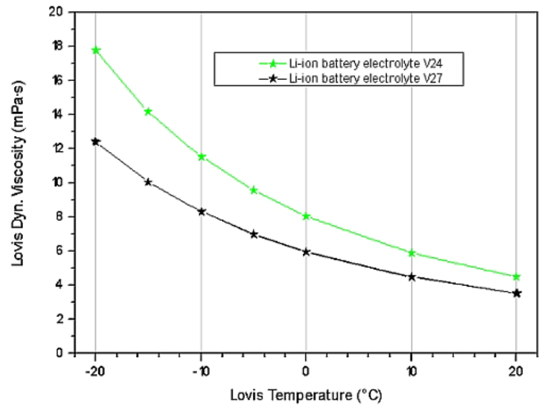

Figure 4: Low temperature profile of two commercially available Li-ion standard electrolytes, purchased from Novolyte Inc.

4.3 Thermal Aging Experiment

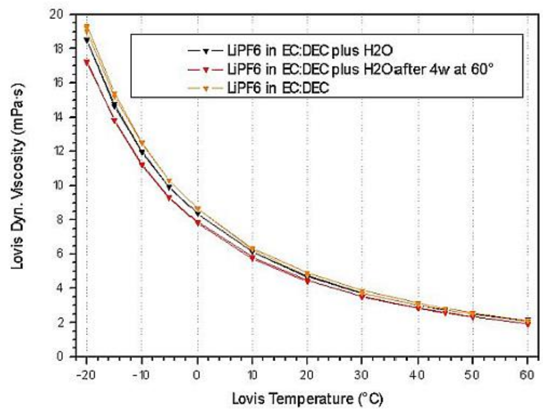

Figure 5: Thermal aging experiment; low temperature profiling of LiPF6 EC:DEC solution newly prepared, plus a certain trace amount of water, and after four weeks of exposition at 60 °C

4.4 Temperature Profile of Li-polysulfide Electrolyte

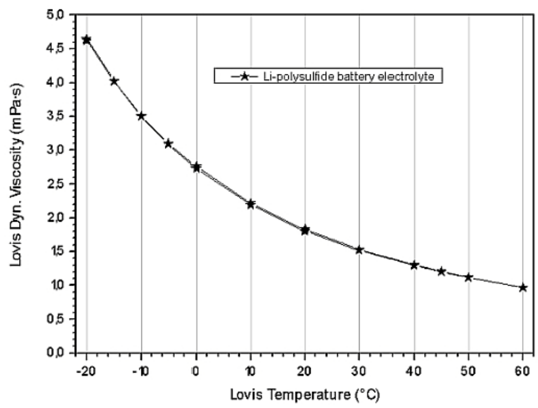

Figure 6: Low temperature profiling a of a newly prepared Li-polysulfide electrolyte for Li-S-batteries

4.5 Checking the Influence of Conducting Salt Concentration for Mg-ion-batteries

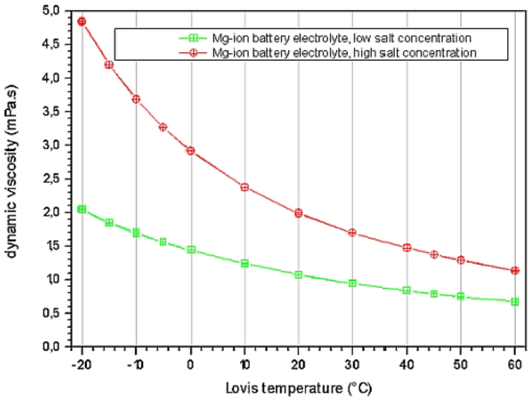

Figure 7: Low temperature profiling of a newly prepared electrolyte with different conducting salt concentrations for Mg-ion batteries

5 Conclusion

By using the Lovis 2000 M/ME equipped with cooling option, it is possible to perform measurements from -20 °C up to +100 °C. In combination with the capillary made of PCTFE even extremely corrosive substances can be measured under hermetically sealed atmosphere. This allows users to measure the viscosity of electrolytes, which might be destroyed or changed in structure by air and/or air humidity.

- The small capillary sizes require only little sample volume (starting from 110 µL).
- The small diameter of the PCTFE capillary (1.62 mm) enables also the measurement of very low-viscosity samples (viscosity range from 0.8 mPa.s to 160 mPa.s).
- The cooling option allows for viscosity measurements down to -20 °C (lower temperatures down to -30 °C are possible on request and depending on ambient conditions).
- The closed system avoids any contamination and evaporation.
- The variable inclination angle of the measurement allows for the variation of the shear rate.
- Lovis 2000 M/ME is highly modular; it can be combined with DMA™ M Density Meters for automated calculation of dynamic and kinematic viscosity. It can also be combined with an Xsample™ sample changer (see Figure 8) for automatic filling and cleaning of the capillary and measurements with high sample throughput.

Figure 8: DMA™ 4500 M plus Lovis ME in combination with Xsample™ 530 Sample Changer

6 References

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Contact Anton Paar GmbH

Tel: +43 316 257-0

support-visco@anton-paar.com |
www.anton-paar.com