Density measurement of lithium-containing electrolytes

Relevant for: Producers of lithium-ion electrolytes and producers of accumulators for the automotive industry and other industries using lithium-ion electrolytes

The density of liquid lithium-ion containing electrolytes dissolved in organic solvents can be monitored during the production and in the final product.

Density measurement represents a fast, reliable and efficient quality control for electrolyte producers, but also for accumulator manufactures.

1 Lithium-containing electrolytes and the automotive market

Lithium-ion accumulators, also frequently referred to as lithium-ion secondary batteries, are to-date among the most frequently used energy sources in electrically powered vehicles. Lithium-ion accumulators offer a high energy density which makes them suitable components in the electric vehicle (**Figure 1**) market.

Figure 1: An electrically powered vehicle – zero emission

These rechargeable batteries consist of a stack of several cells, each of them containing two electrodes and an electrolyte containing lithium (Li) ions as charge carriers. The lithium-ion (Li^+) carries one positive charge.

Secondary batteries containing Li-ion electrolytes are suitable to match the growing demand of alternatives to combustion engines. These batteries are not only used for cars, but also for all kinds of electronic devices such as mobile phones, tablets, digital cameras or flashlights.

Many factors drive the growth of the secondary battery market. Among them are the increasing acceptance of electrical vehicles to reduce the carbon footprint, and the increasing interest in alternative energy sources. On top of that, the continuous growth of automotive sales generates a high demand for replacement automotive batteries.

2 The role of electrolytes in lithium-ion cells

The electrolyte plays a key role in all kinds of batteries and accumulators. The Li-ions in the electrolyte make the charge transfer between anode and cathode possible. Lithium-containing salts are used for this purpose. The most commonly used salt in Li-ion electrolytes is lithium hexafluorophosphate ($LiPF_6$), but also other salts such as lithium tetrafluoroborate ($LiBF_4$) apply [1].

When brought in contact with water, lithium is highly reactive. This is the reason why the anhydrous lithium salts are imbedded in matrices that are composed of organic solvents and may also be accompanied by some additives.

3 A little bit of electrochemistry

Every cell of the battery stack contains two electrodes, a cathode and an anode, plus the electrolyte, typically composed of solvents and lithium-ions to allow the movement of electric charge between the electrodes.

Lithium salts can easily be turned into Li^+ ions transferring charge in-between electrodes. The most common anode material is graphite, while the cathode material is lithium metal oxide ($LiMO_2$) in most cases, M being Nickel, Manganese, Cobalt, (NMC) or a combination such as e.g. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [1]. Both electrodes contain lithium atoms which are turned into ions that, migrating from one electrode to the other, release or accept electrons (e^-) and close the electric circuit during charge and discharge, respectively. The cell reactions are given in **Figure 2** [1].

Positive: $$LiMO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Li_{1-x}MO_2 + x\,Li^+ + x\,e^-$$

Negative: $$C + y\,Li^+ + y\,e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Li_yC$$

Overall: $$LiMO_2 + x/y\,C \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} x/y\,Li_yC + Li_{1-x}MO_2$$

Figure 2: Electrode reactions in the most common Li-ion cells

4 Density measurement of Li-ion electrolytes

In Li-ion accumulators, the Li-containing salt is dissolved in an organic solvent such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC). **Table 1** summarizes a few of their characteristics [2].

Table 1. Characteristics of a few commonly used solvents in Li-ion electrolytes

Property	EC	DMC	DEC	EMC
Chemical formula	$C_3H_4O_3$	C_3H_6O3	$C_5H_{10}O_3$	$C_4H_8O_3$
Molar mass [g/mol]	88.062	90.078	118.132	104.10
Appearance	White to yellow solid	Clear liquid	Clear colorless liquid	Liquid
Density [g/cm³]	1.32 (40 °C)	1.07 (20 °C)	0.975 (25 °C)*	1.01 (20 °C)

* Sigma-Aldrich

In Li-ion secondary batteries, mixtures of these carbonates are used as non-aqueous electrolytes, sometimes also in combination with additives to optimize the electrolyte's performance, e.g. to improve its surface tension for better contact with the electrode material [3]. Depending on the composition, the density of the electrolyte varies.

The density of the electrolyte for Li-ion accumulators does not change as a function of charge and discharge. Thus, independent of the state of charge, the density is a reliable means to ensure that the composition of the electrolyte corresponds to requirements and specifications.

Li-ion electrolytes usually contain two or more of the solvents that are listed in **Table 1**. Literature data of densities of various electrolytes are summarized in **Table 2** [4].

Table 2. Densities of 1 M $LiPF_6$ in solvent mixtures

Electrolyte composition	Density [g/mL]
1M LiPF6 in EC:DMC (1:1 vol.%)	1.289 (20 °C)
1M LiPF6 in EC:DEC (1:1 vol.%)	1.242 (20 °C)
1M LiPF6 in EC:EMC (1:1 vol.%)	1.26 (20 °C)
1M LiPF6 in EC:DEC:DMC (1:1:1 vol.%)	1.216 (20 °C)
1M LiPF6 in EC:EMC:DMC (1:1:1 vol.%)	1.219 (20 °C)

It can be seen even more easily in **Figure 3** that the densities vary according to the electrolyte composition.

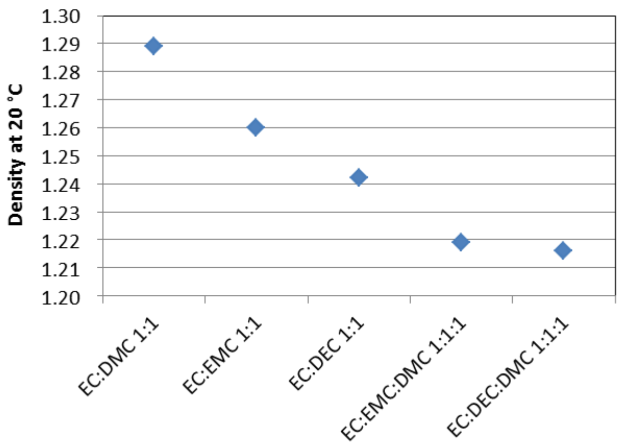

Figure 3: Densities of $LiPF_6$ in different solvent mixtures

Thus, the kind of electrolyte can be determined based on density measurement.

5 Suitable instruments for various needs

5.1 DMA 35

The portable DMA 35 density meter (**Figure 4**) is the best choice for on-site measurements.

The light-weight design makes DMA 35 the ideal companion for applications requiring an accuracy of ± 0.001 g/cm³ and a repeatability of ± 0.0005 g/cm³.

Figure 4: The portable DMA 35 density meter

5.2 DMA 501 and DMA 1001

The robust stand-alone laboratory density meters DMA 501 and DMA 1001 (**Figure 5**) with an accuracy of ± 0.001 g/cm³ or ± 0.0001 g/cm³, respectively, and repeatability of ± 0.0002 g/cm³ or ± 0.00005 g/cm³, respectively, provide the U-View™ and FillingCheck™ features as well as a full-range viscosity correction and PCAP touch screen.

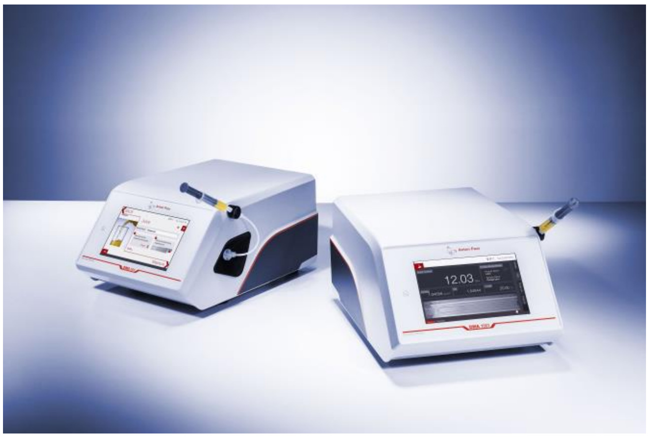

Figure 5: The density meters DMA 501 and 1001

5.3 DMA 4100/4500/5000 M

The family of DMA M density meters (**Figure 6**) represents the best solution in case of multiple sample analysis as these instruments can be operated in combination with an Xsample sample changer. Depending on the required accuracy, the density meters DMA 4100 M and DMA 4500 M offer themselves for fast and accurate analyses.

DMA 5000 M is the high-end solution for the highest requirements, its accuracy of 0.000007 g/cm³ is unmatched on the market.

Figure 6: The DMA M family

6 With an eye on the future

DMA M density meters are well-proven master instruments for several instrument combinations if the need for additional quality parameters should arise in the future. Instruments such as a viscosity meter can be connected to a DMA M density meter without problems at any later stage. In case of combinations with other instruments or measuring modules, all parameters are measured simultaneously on the same sample – this avoids erroneous conclusions due to variations in sample composition. In addition, the combination with various Xsample sample changer models is possible for high sample throughputs.

7 Benefits of density measurement

For monitoring these electrolyte solutions, density measurement is a reliable method for

- quick quality checks of raw materials,
- final density control for certificates,
- rapid checks to ensure that the salt was dissolved properly, completely and in the right concentration, and
- quality control for the customers (electrolyte and battery manufacturers).

8 References

[1] Linden's Handbook of Batteries 4th edition, McGraw-Hill 2011

[2] Wikipedia.org

[3] www.batterieforum-deutschland.de

[4] MSDS Solvionic; France

[5] Anton Paar Application Report XPAIA012EN

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