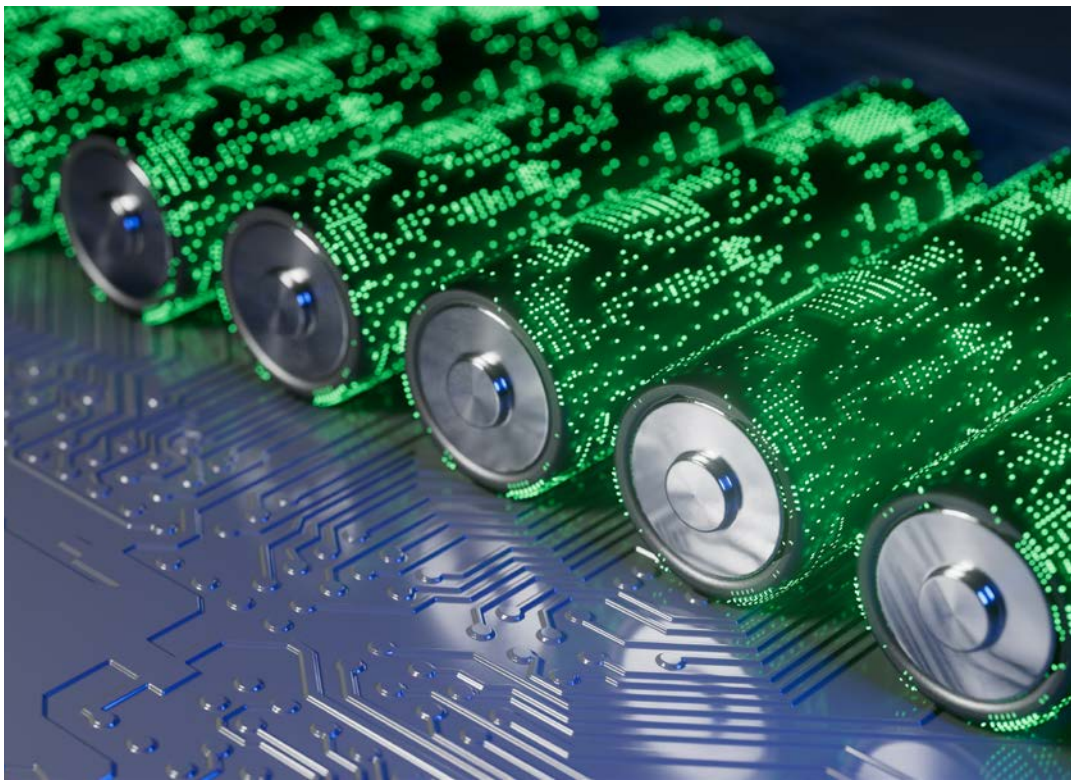
Titration Application Note

KF titration of LIB Electrolyte with HYDRANAL™ NEXTGEN FA Reagents

Lithium-ion batteries make our modern life possible delivering the necessary power to all kind of portable devices ranging from wireless headphones, smartphones, e-readers and notebooks to drones, e-scooters and even battery electric vehicles. With recent advances in battery research, the range of possible use-cases expands further, and Li-ion batteries already power small airplanes and ferries and are utilized to stabilize the electrical power gird in times of high demand.

Research showed that small modifications to the individual components of the cell have a large impact in the overall performance of the battery. As such, the electrolyte has a direct influence on the reversibility, life cycle and safety of the battery cell.[1]



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Introduction

Cyclic and non-cyclic organic carbonates (e.g. ethylene carbonate (EC) or ethyl methyl carbonate (EMC)) are commonly employed as electrolyte solvents and fluorinated lithium salts – e.g. lithium hexafluorophosphate ($LiPF_6$) or lithium fluorosulfonyl imide (LiFSI) – as electrolyte salts. However, this category of electrolyte salts is known to undergo hydrolysis in the presence of residual water forming highly toxic and corrosive hydrofluoric acid (HF), which can have a detrimental effect on the cell. Therefore, it is of utmost importance that the residual water level in the electrolyte is tightly controlled. Li-ion electrolytes usually contain additives to improve the life cycle of the battery cell such as vinylene carbonate, fluoroethylene carbonate and different lithium borate salts. However, these additives react with alcoholic components of standard KF reagents as well as methanol-free KF reagents causing either iodine-consuming or water-releasing side reactions. This renders it rather difficult to determine an accurate and precise water content in electrolytes. To solve this issue, Honeywell developed a purpose-built KF reagent, which enables water determination in Li-ion battery electrolytes with and without additives. Herein, a method to determine the water content in lithium battery electrolyte with Hydranal™ NEXTGEN Coulomat A-FA and C-FA is described using coulometric KF titration with direct injection.

Chemistry

KF Reaction: $MeSO_3H + RN{\cdot}SO_2 + 2\ RN + I_2 + H_2O \rightleftharpoons [RNH]MeSO_3SO_3 + 2\ [RNH]I$

Solutions and Chemicals

Anolyte: Hydranal™ NEXTGEN Coulomat A-FA (34471)
Catholyte: Hydranal™ NEXTGEN Coulomat C-FA (34470)
Standard: HYDRANAL™ – Water Standard 0.1 PC (34446), based on propylene carbonate (water content 0.1 mg/g = 0.01%)
Sample: 1.0 M $LiPF_6$ in ethylene carbonate (EC) / ethyl methyl carbonate (EMC), 50/50% v/v, battery grade (commercially available electrolyte)
Analyte: Water, H_2O, M = 18.01 g/mol

Instruments and Accessories

- Compact Line C30SD (30252663)
- XPR205DR Analytical balance (30355415)
- DM143-SC Double pin platinum electrode (51107699)
- Generator electrode with diaphragm (51108751)
- Plastic syringes, needles

C30S coulometric KF titrator

Preparations and Procedure

Titration Cell

- Prior to performing measurements, all components of the titration cell (glass cell, stir bar and generator electrode) have to be dried in the oven at 70–80°C for several hours.
- Fill the generator electrode, cathodic chamber, with 5 ml Hydranal NEXTGEN Coulomat C-FA (catholyte). To prevent any side reactions on the cathode, a generator electrode with diaphragm must be used.
- The anode compartment should be filled with 100 ml Hydranal NEXTGEN Coulomat A-FA (anolyte) to a level, which is a few millimeters above the catholyte level.

Method

- Method M882 is a pre-defined Mettler method to measure the water content in electrolytes. This method performs a pre-titration to remove the residual water and subsequently switches into standby mode. The measurements should only be started when the drift is lower than 10 µg/min and stable (no abrupt fluctuations).
- Prior to and at the end of a sample sequence, a water standard 0.1 PC (1–1.5 ml) should be injected to confirm the recovery and ensure the reliability of test results.

Sample

- Rinse the syringe with about 1 ml of the sample to remove any residual water. Discard the rinsing solution and wipe the needle dry.
- Fill the syringe with the sample to its maximal volume. Prior to removing the air bubble inside the syringe, use it to homogenize the sample by flipping the syringe upside down and back. Thereafter, remove the air bubble and place the syringe on the balance and tare.
- Start the measurement by pressing: "Start Sample" on the display of the titrator.
- Inject an aliquot of the sample (~1.5 ml) to the titration cell and press "ok".
- The injected mass is obtained by back weighing of the sample syringe.

Results and Discussion

The sample is very hygroscopic and takes up water from the environment during the analysis procedure leading to a positive trend in the determined water level. Therefore, it would be recommended to perform measurements inside a dry glovebox or using airtight syringes (5, 10 ml). Furthermore, the solubility of $LiPF_6$ in Hydranal NEXTGEN Coulomat A-FA limits the amount of electrolyte sample that can be analyzed to max. 18 ml.

The results are displayed in the table below:

	Mass (g)	Content (ppm)	Recovery (%)	Mean Content (ppm)	SD (ppm)
Standard	1.662	105.7	96.9		
1	2.240	4.3			
2	1.897	6.0		5.0	0.7
3	1.909	4.6			
4	1.887	10.3			
5	2.444	10.4			
6	2.286	8.7		9.9	0.6
7	1.879	10.4			
8	1.808	9.8			
Standard	1.461	102.3	96.5		

Samples were injected from two withdrawals of the same bottle of electrolyte. The first three injections were from the first withdrawal with the mean water content of 5.0 ppm and the standard deviation (SD) of 0.7 ppm.

The injections 4–8 were carried out from the second withdrawal with the mean water content of 9.9 ppm and the SD of 0.6 ppm.

According to the certificate of analysis, the used batch of electrolyte contained 6 ppm of water (specified limit: <15 ppm). The measured values of the first withdrawal were very close to the certified value. The high hygroscopicity of the electrolyte lead to increased water levels in the results of the second withdrawal. However, the values still fulfilled the specifications.

Waste Disposal and Safety Measures

Dispose the content of the titration vessel in a special waste container for KF reagents.

References

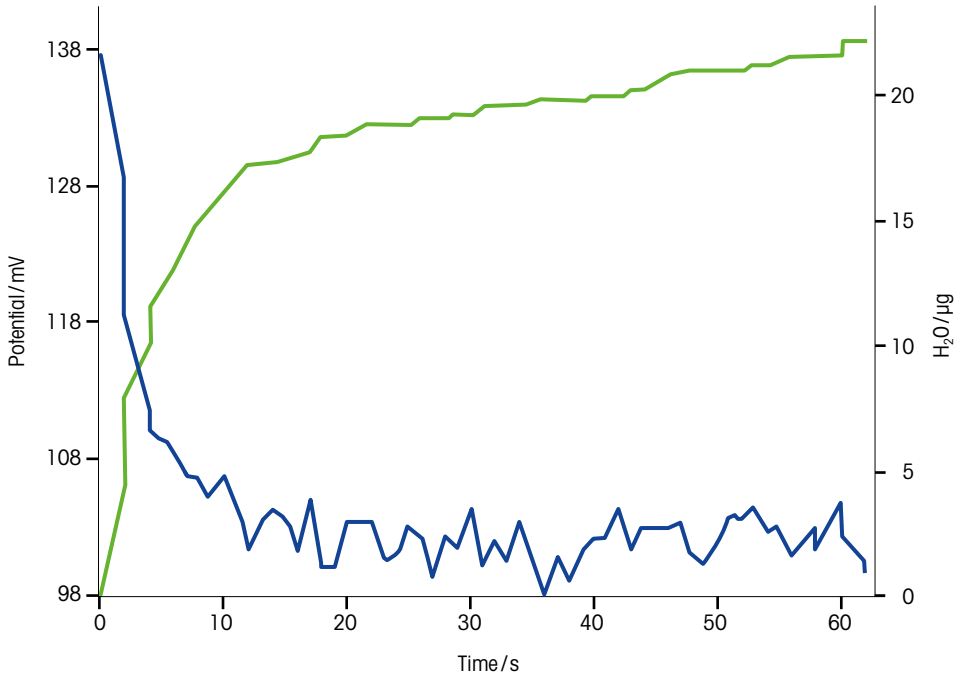
[1]. M. Li, J. Lu, Z. Chen, K. Amine, Adv. Mater. 2018, 30, 1800561.

Further information

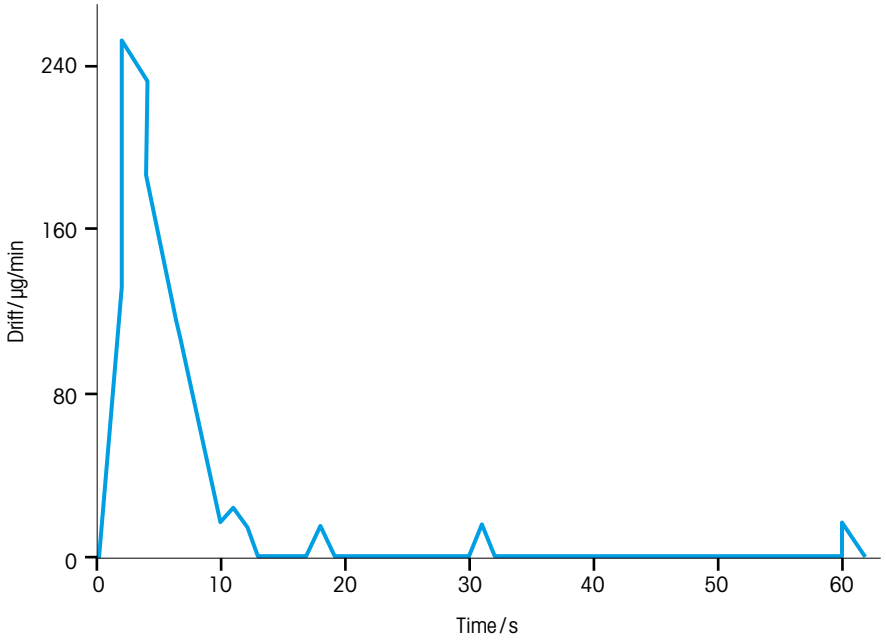
- **www.mt.com/int/en/home/products/Laboratory_Analytics_Browse/Product_Family_Browse_titrators_main/Karl_Fischer_Titration.html**

Measured Values

A



B



A: potential (dark blue), accumulated water (green) and B: drift (blue) of electrolyte sample 2/8 measured with new KF reagents (data in table below).

Consumption [C]	Potential [mV]	Accumulated H_2O [µg]	Drift [µg/min]	Time [s]
0	137.8	0	0	0
49.7	128.8	4.6	136.2	2
84.1	118.9	7.9	252.7	2
109.6	111.5	10.2	232.4	4
124.6	110.3	11.6	187.3	4
141.1	109.1	13.2	129.5	6
151.6	106.8	14.2	95.1	7
160.7	106.7	15	70	8
168.2	105.2	15.7	41.4	9
174.3	107.1	16.3	17	10
180.4	104.9	16.8	25.4	11
…	…	…	…	…
229.7	103.1	21.4	0	55
231.2	100.8	21.6	0	56
231.3	103	21.6	0	58
231.8	101.5	21.6	0	58
232.3	105	21.7	0	60
238.3	102.3	22.2	17	60
238.4	100.5	22.3	0	62
238.4	99.7	22.3	0	62

Method M882

001 Title

Type	KF Coulometric
ID	M882
Title	KF titration of LIB Electrolyte with HYDRANAL™ NEXTGEN FA Reagents

002 Sample

Number of IDs	1
ID 1	Electrolyte
Entry type	Weight
Lower limit	0.0 g
Upper limit	5.0 g
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0 °C
Entry	After addition
Open series	Yes

003 Titration stand

Type	KF stand
Titration stand	KF stand
Source for drift	Online
Max. start drift	60 µg/min

004 Mix time

Duration	5 s

005 Titration (KF Coul) [1]

Sensor	
Type	Polarized
Sensor	DM143-SC
Unit	mV
Indication	Voltametric
IPol	5.0 µA
Stir	
Speed	60%
Control	
Endpoint	100.0 mV
Controlband	350.0 mV
Rate	Normal
Generator current	Automatic
Termination	
Type	Drift stop relative
Drift	1.0 µg/min
Min. time	40 s
Max. time infinite	Yes

006 Calculation R1

Result	Content
Result unit	ppm
Formula	R1=(ICEQ/10.712–TIME *DRIFT)/(C*m)
Constant C	C=1
Decimal places	3
Result limits	No
Extra statistical functions	No
Send to buffer	No
Condition	No

007 Record

Report template	KF sample report

008 End of Sample

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