ACCURATE WATER DETERMINATION IN LITHIUM-ION BATTERIES WITH HYDRANAL™ NEXTGEN COULOMAT A-FA AND C-FA

World's First Commercially Available Karl Fischer Titration Reagents
Free of Alcohol and Free of Imidazole

Honeywell

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INTRODUCTION

Karl Fischer (KF) titration is the preferred method for testing water content in lithium-ion battery (LiB) electrolyte samples due to its accuracy and reliability. Modern electrolyte formulations created the need for new KF reagents suitable for more challenging requirements.

In 1991, Sony Co. commercialized the world's first lithium-ion battery (LiB). Since then, LiBs have been used to store energy in a wide variety of devices, and their market continues to grow. In recent years, significant commercial and academic progress has been made. Research has shown to improve performance and expand applications. Even small changes in the composition of anode, cathode, or electrolyte material can alter the overall performance of the battery. In particular, the electrolyte and its additives have important implications for the properties of lithium- ion batteries in terms of lifecycle limitations, capacity for reversibility, and safety.[1]

Cyclic and non-cyclic carbonates are often used as electrolyte solvent. The use of keto-esters has also been reported.[2,3] Well-known additives, including vinylene carbonate (VC), fluoroethylene carbonate (FEC), and lithium borate salts such as lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB) and lithium tetrafluoroborate ($LiBF_4$), improve the lifecycle of LiBs, especially at higher temperature, and keeps the internal resistance low with use and age.[4]

However, most LiBs contain fluorinated lithium salts, [e.g., lithium hexafluorophosphate ($LiPF_6$) and/or lithium fluorosulfonyl imide, (LiFSI)] , that are reactive towards trace amounts of moisture in the electrolyte solution. The $LiPF_6$ salt is known to undergo hydrolysis, producing hydrofluoric acid (HF), which is a highly toxic and corrosive gas that can damage the inside of the battery[5,6]. While LiFSI is expected to be less susceptible to this degradation, such reactions are also expected.

1. M. Li, J. Lu, Z. Chen, K. Amine, *Adv. Mater.* ***2018,*** 30, 1800561
2. S. Kondou, M. L. Thomas, T. Mandai, K. Ueno, *Phys. Chem. Chem. Phys.*, ***2019,*** 21, 5097.
3. US patent US8795905B2
4. N. Choi, J. Han, S. Ha, I. Parka, C. Back, *RSC Adv.,* ***2015,*** 5, 2732.
5. K. Tasaki, K. Kanda, S. Nakamura and M. Ue, *J. Electrochem. Soc.*, ***2003,*** 150, A1628.
6. U. Karst and S. Nowak, *J. Power Sources*, ***2013,*** 242, 832.

WATER DETERMINATION IN LIB SAMPLES

Humidity plays a dominant role in the quality and stability of batteries. Most batteries require water-free electrolytes, because water can be electrolyzed to give H_2 and O_2 gases that can cause the battery to explode.[7]

Therefore, to ensure product quality and safety, low water content is one of the key requirements for LiBs. To fulfill this requirement, the ability to perform highly accurate water determinations is critical.

For low water content samples, coulometric Karl Fischer (KF) titration is the method of choice. However, the main solvent in all standard KF reagents is alcohol, usually methanol. Even special methanol-free reagents contain other alcohols. The huge disadvantage of alcohols is their ability to undergo side reactions with the additives used in many LiB electrolytes. That is why it has been difficult or even impossible to measure water content in most prominent LiB electrolytes that contain additives like VC, FEC, and borates such as LiBOB and LiDFOB. Typical issues encountered when using standard alcoholic KF reagents for different LiB samples are listed in Table 1. An example titration of VC sample in alcoholic KF reagent is shown on Fig. 1.

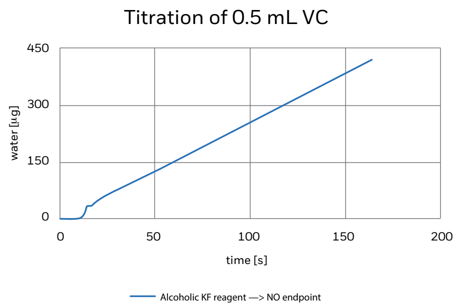

Fig. 1. Titration of 0.5 mL VC. No end point reached. Titration has been stopped manually.

SAMPLE	AS RAW MATERIAL	AS ADDITIVE	COMMENT
Unsaturated compounds e.g. VC, vinyl acetate	No or fading end point (see Fig. 1). Accurate water determination is impossible.	Increasing drift. Decreasing accuracy of titration.	Iodine-consuming side reaction occurs.
FEC	Causes fewer problems compared to VC when sample size is small. Otherwise, no or fading end point.	Causes fewer problems if the absolute water content in the sample is low.	Can be titrated with low water content in small portions; however, small sample size increases weighing error.
Borates e.g. LiBOB, LiDFOB	Accurate water determination is impossible.	Long titration with highly overdetermined results. Note: end point can be reached, but giving incorrect result (see Fig. 2).	Water-releasing side reaction occurs.
Ketones e.g. acetone	No or fading end point. Accurate water determination is impossible.	Long titration with highly overestimated results. No or fading end point. Increasing drift.	Water-releasing side reaction occurs. Acetone and diketones are decomposition products in LiB electrolytes containing propylene carbonate (PC). [8]

Table 1. Typical issues encountered when using standard alcoholic KF reagents.

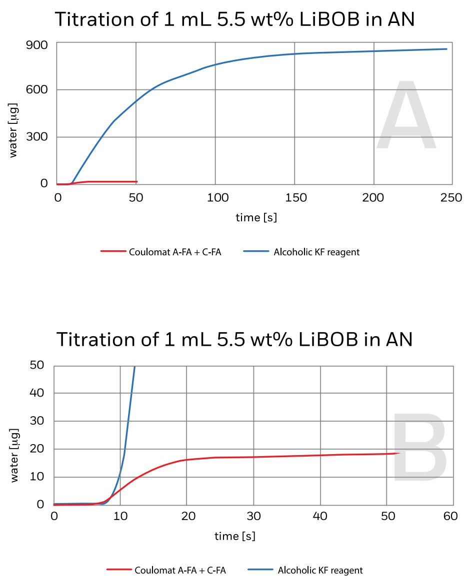

Fig. 2. A) and B) Titration of 1 mL 1 M $LiPF_6$ in EC/DMC with 5.5 wt% LiBOB in alcoholic KF reagent (blue line) and in alcohol-free reagent Coulomat A-FA/C-FA (red line). Both titrations give stable endpoints, but only Coulomat A-FA/C-FA provides the correct result (B is a zoomed frame of A).

7. A. Eftekhari, *Adv. Energy Mater.* ***2018,*** 8, 1801156.
8. E. G. Leggesse, R. T. Lin, T.-F. Teng, C.-L. Chen, J.-C. Jiang, *J. Phys. Chem. A,* ***2013,*** 117, 7959.

HYDRANAL™ NEXTGEN COULOMAT A-FA AND C-FA

Hydranal NEXTGEN Coulomat A-FA (anolyte) and C-FA (catholyte) are the first commercially available non-alcoholic KF reagents that are also free of imidazole, and allow accurate and reliable titrations of many LiB electrolytes and additives. Feasibility comparison of Coulomat A-FA and C-FA with standard alcoholic KF reagents for different types of LiB electrolytes and pure additives is shown in Table 2. An example titration of LiB electrolyte containing borates in alcoholic KF reagent and Hydranal NEXTGEN Coulomat A-FA and C-FA is shown on Fig. 2.

SOLUBILITY

Hydranal NEXTGEN Coulomat A-FA and C-FA are free of methanol and other alcohols. Instead of alcohols, acetonitrile is used as the main solvent. The solubility properties of methanol and acetonitrile differ from each other. Many polar salts such as $LiPF_6$ dissolve better in methanol, whereas more non-polar samples dissolve better in acetonitrile.

The solubility of 5 wt% LiBOB solution in PC in Hydranal NEXTGEN Coulomat A-FA is very high, whereas the solubility limit of 1 M $LiPF_6$ solution in PC in 100 mL Hydranal Coulomat A-FA is around 18 mL. After adding approx. 18 mL, the reagent gets cloudy and salt starts to precipitate. Often, it is possible to do some further titrations without any problems, but we highly recommend changing the reagent when it gets cloudy. Otherwise, the generator electrode may be damaged.

VESSEL TYPE

Hydranal NEXTGEN Coulomat A-FA and C-FA will provide best results in a coulometric cell with diaphragm. In cells without diaphragm, the results may be increased by approximately 10%.

WATER STANDARDS

Many water standards contain alcohols such as 1-butanol or 1-methoxy-2-propanol which can react with many LiB electrolytes causing drift increase and erroneous water content results. Therefore, it is very important to use **only alcohol-free water standards** for the verification of the titration cell.

Hydranal offers four water standards that are free of alcohols:

- 34426 HYDRANAL-CRM Water Standard 1.0 (water content 1.0 mg/g = 0.1%), based on anisole and propylene carbonate
- 34828 HYDRANAL-Water Standard 1.0 (water content 1.0 mg/g = 0.1%), based on anisole and propylene carbonate
- 34847 HYDRANAL-Water Standard 0.1 (water content 0.1 mg/g = 0.01%), based on o-xylene
- 34446 HYDRANAL-Water Standard 0.1 PC (water content 0.1 mg/g = 0.01%), based on propylene carbonate

It is important to notice that water standards based on anisole cannot be used in combination with borate-containing samples (e.g. LiBOB), because anisole is able to decompose into alcohols (phenol and methanol). It is highly recommended to use 34446 Hydranal-Water Standard 0.1 PC for all samples, because it has the best solubility for LiB salts and is stable (no decomposition).

SAMPLE	COULOMAT A-FA + C-FA	ALCOHOLIC KF REAGENTS
LiB electrolyte with VC/FEC	+	o
LiB electrolyte with LiBOB	+	-
LiB electrolyte with LiDFOB	+	-
Pure VC	+	-
Pure FEC	+	o
Pure LiBOB	+	-
Pure LiDFOB	+	-
Ketones	+	-

+ accurate titration, suppressed side effects
o limited titration (possible only for small amount of sample)
- no accurate titration possible (side reactions, increasing drift or inaccurate results)

VC = vinylene carbonate
FEC = fluoroethylene carbonate
LiBOB = lithium bis(oxalate)borate
LiDFOB = lithium difluoro(oxalato)borate

Table 2. Comparison of Hydranal NEXTGEN Coulomat A-FA + C-FA with standard alcoholic KF reagents.

EXAMPLE TITRATION RESULTS

INDIVIDUAL SAMPLES

In the battery production process, in order to guarantee high quality and safety, the water content should be measured not only in the final electrolyte, but also in raw materials. Different electrolytes and different raw materials were tested for water content using Hydranal NEXTGEN Coulomat A-FA and C-FA. Results are shown in Tables 3 and 4.

In all tested electrolytes, the water content was measured with high accuracy. Among electrolyte raw materials, only in tris(trimethylsilyl) phosphite and tris(trimethylsilyl) borate the titration was not possible due to other side effects that cannot be suppressed. In all other tested raw materials, the water content was measured with high accuracy.

SAMPLE	MEAN WATER CONTENT (N = 5-6) [ppm]	ABS. STD. DEV. [ppm]
1 M $LiPF_6$ in EC/DEC (50/50 vol%) + 4 wt% VC	6.9	1.1
1 M $LiPF_6$ in EC/DMC (50/50 vol%) + 10 wt% $LiBF_4$	146.7	1.1
1 M $LiPF_6$ in EC/DMC (50/50 vol%) + 5 wt% LiBOB	3.3	0.5
1 M $LiPF_6$ in EC/EMC/DMC (20/40/40 vol%)		
+ 2 wt% $LiPO_2F_2$ + 4 wt% VC	4.9	1.9
1 M $LiPF_6$ in EC/DEC/DMC (20/30/40 vol%)		
+ 2 wt% $LiPO_2F_2$ + 4 wt% VC	3.5	0.9
5 wt% VC + 5 wt% FEC + 2 wt% LiBOB + 2 wt% lithium nonafluoro-1-butanesulfonate in AN	33.8	0.5
5 wt% LiDFOB in AN/PC (50/50 vol%)	71.2	0.5
5 wt% LiDFOB + 5 wt% succinic anhydride in AN	88.9	0.5
EC = ethylene carbonate DEC = diethyl carbonate EMC = ethyl methyl carbonate DMC = dimethyl carbonate VC = vinylene carbonate AN = acetonitrile PC = propylene carbonate LiBOB = lithium bis(oxalate)borate		

Table 3. Titration of LiB electrolytes with Hydranal NEXTGEN Coulomat A-FA and C-FA.

SAMPLE	MEAN WATER CONTENT (N = 4-6) [ppm]	ABS. STD. DEV. [ppm]
LITHIUM SALTS		
Lithium acetate[9]	102.3	1.9
Lithium bis(oxalato)borate (LiBOB)[9] (over molecular sieves)	10.0	0.2
Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)[9]	13.7	4.2
Lithium difluoro(oxalato)borate (LiDFOB)[9]	77.4	0.7
Lithium nonafluoro-1-butanesulfonate[9]	4.3	2.4
CARBONATES		
Fluoroethylene carbonate (FEC)	33.1	0.2
Propylene carbonate (PC)	98.8	0.5
Vinylene carbonate (VC)	88.2	0.1
SULFUROUS COMPOUNDS		
Allyl methyl sulfone	1571.4	20.4
Ethylene sulfite	466.5	0.9
Ethylene sulfite (over molecular sieves)	27.3	0.1
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	694.4	2.9
1,3-Propanesultone[9]	31.7	0.2
2-Propynyl methanesulfonate	575.2	5.7
KETONES		
Acetone (over molecular sieves)	7.2	0.5
Acetylacetone	561.9	1.1
2-Butanone (over molecular sieves)	6.3	0.5
Methyl acetoacetate	27.6	0.6
Methyl levulinate	71.4	0.5
4-Methy-2-pentanone	188.9	0.2
OTHER		
Acetonitrile	8.2	0.2
Adiponitrile	13638.8	73.9
Allyl acetate	368.1	3.7
Tert-Amylbenzene	124.3	0.2
Phenylcyclohexane	95.8	0.2
Tris(trimethylsilyl) borate	Not possible	
Tris(trimethylsilyl) phosphite	Not possible	
Vinyl acetate	56.8	0.4

Table 4. Titration of LiB electrolyte raw materials with Hydranal NEXTGEN Coulomat A-FA and C-FA.

9. 5 wt% in acetonitrile

SERIES OF SAMPLES

One of the main advantages of the new Hydranal NEXTGEN Coulomat A-FA and C-FA reagents is the possibility of measuring successively many different LiB additive and electrolyte samples in one vessel filling. To check the accuracy of obtained results, water standard samples were tested for water recovery before each series of same samples. Additionally, the drift value was controlled before each titration. Results of such measurement series are shown in Tables 5 and 6. In all cases, the obtained water content results had high accuracy, and water recovery for the 102 ppm water standard was in the range of 97-103%. [10]

NO.	SAMPLE	WATER MEASURED [ppm]	WATER MEASURED [μg]	TITRATION TIME [s]	START DRIFT [μg/min]	WATER RECOVERY [%]
1	**1 mL water standard 102 ppm**	105.3	127.8	55	4.3	**103**
2	**1 mL VC**	88.1	115.9	59	4.2	
3	**1 mL VC**	88.4	120.3	55	4.9	
4	**1 mL VC**	88.2	119.9	55	5.2	
5	**1 mL VC**	88.3	118.6	59	5.1	
6	**1 mL VC**	88.2	114.2	55	5.7	
7	**1 mL water standard 102 ppm**	105.0	126.4	58	5.9	**103**
8	**1 mL FEC**	32.9	46.6	56	3.1	
9	**1 mL FEC**	33.2	49.6	53	3.1	
10	**1 mL FEC**	33.4	50.3	56	3.1	
11	**1 mL FEC**	33.0	48.7	56	3.3	
12	**1 mL FEC**	33.1	47.3	57	3.3	
13	**1 mL water standard 102 ppm**	104.4	126.9	59	3.2	**102**
14	**1 mL 2-Propynyl methanesulfonate**	566.4	698.4	81	3.0	
15	**1 mL 2-Propynyl methanesulfonate**	570.5	720.7	80	3.8	
16	**0.5 mL 2-Propynyl methanesulfonate**	576.8	374.3	72	4.7	
17	**0.5 mL 2-Propynyl methanesulfonate**	577.1	371.2	69	4.7	
18	**0.5 mL 2-Propynyl methanesulfonate**	578.3	366.4	66	4.7	
19	**0.5 mL 2-Propynyl methanesulfonate**	582.0	350.1	66	4.4	
20	**1 mL water standard 102 ppm**	98.9	120.4	63	4.7	**97**
21	**1 mL Allyl methyl sulfone**	1535.5	1848.2	113	4.5	
22	**0.5 mL Allyl methyl sulfone**	1575.0	939.9	86	6.2	
23	**0.5 mL Allyl methyl sulfone**	1579.6	925.0	87	6.3	
24	**0.5 mL Allyl methyl sulfone**	1585.3	916.0	86	5.8	
25	**0.5 mL Allyl methyl sulfone**	1581.6	960.7	89	6.5	
26	**1 mL water standard 102 ppm**	101.8	123.3	67	6.7	**100**
27	**1 mL 1 wt% Lithium acetate in AN**	103.6	68.8	66	5.8	
28	**1 mL 1 wt% Lithium acetate in AN**	101.3	80.4	67	5.6	
29	**1 mL 1 wt% Lithium acetate in AN**	104.8	80.9	72	4.0	
30	**1 mL 1 wt% Lithium acetate in AN**	100.4	78.1	68	5.4	
31	**1 mL 1 wt% Lithium acetate in AN**	101.2	75.9	72	5.1	
32	**1 mL water standard 102 ppm**	103.3	127.3	78	4.8	**101**

Table 5. Successive titrations of LiB additives in one vessel filling with 100 mL Hydranal NEXTGEN Coulomat A-FA and 5 mL Hydranal NEXTGEN Coulomat C FA.

10. For good results, the water recovery of a 100 ppm water standard should be in the range of 90-110%.

NO.	SAMPLE	WATER MEASURED [ppm]	WATER MEASURED [µg]	TITRATION TIME [s]	START DRIFT [µg/min]	WATER RECOVERY [%]
1	**1 mL water standard 102 ppm**	98.6	120.6	58	2.8	**97**
2	**1 mL 5 wt% LiBOB in AN**	10.1	6.8	42	2.2	
3	**1 mL 5 wt% LiBOB in AN**	10	7.9	53	2.3	
4	**1 mL 5 wt% LiBOB in AN**	10.2	8.1	42	2.1	
5	**1 mL 5 wt% LiBOB in AN**	9.6	7.7	47	2.2	
6	**1 mL 5 wt% LiBOB in AN**	10.2	7.3	47	2.3	
7	**1 mL water standard 102 ppm**	99.4	120.9	66	2	**97**
8	**1 mL 5 wt% LiDFOB in AN/PC (50/50 vol%)**	70.4	60.1	69	2	
9	**1 mL 5 wt% LiDFOB in AN/PC (50/50 vol%)**	71.4	58.7	64	1.9	
10	**1 mL 5 wt% LiDFOB in AN/PC (50/50 vol%)**	71.2	59.8	63	1.8	
11	**1 mL 5 wt% LiDFOB in AN/PC (50/50 vol%)**	71.2	56.2	62	1.8	
12	**1 mL 5 wt% LiDFOB in AN/PC (50/50 vol%)**	71.8	57.2	61	1.5	
13	**1 mL water standard 102 ppm**	99.5	119.8	68	1.6	**98**
14	**1 mL LiB electrolyte 1**	147.3	234.5	137	1.5	
15	**1 mL LiB electrolyte 1**	148.2	202.6	71	4.1	
16	**1 mL LiB electrolyte 1**	145.7	194.7	71	3.8	
17	**1 mL LiB electrolyte 1**	145.8	192.6	77	3.3	
18	**1 mL LiB electrolyte 1**	146.5	185.7	73	2.9	
19	**1 mL water standard 102 ppm**	100.5	121.4	66	2.6	**99**
20	**1 mL LiB electrolyte 2**	3.3	4.5	45	1.6	
21	**1 mL LiB electrolyte 2**	2.6	3.4	39	2.5	
22	**1 mL LiB electrolyte 2**	3.2	4.1	45	2.2	
23	**1 mL LiB electrolyte 2**	4.1	5.3	45	2.4	
24	**1 mL LiB electrolyte 2**	3.2	3.9	39	2.3	
25	**1 mL water standard 102 ppm**	99.8	113.9	67	2.5	**98**

LiB electrolyte 1 = 1 M $LiPF_6$ in EC/DMC (50/50 vol%) + 10 wt% $LiBF_4$
LiB electrolyte 2 = 1 M $LiPF_6$ in EC/DMC (50/50 vol%) + 5 wt% LiBOB

Table 6. Successive titrations of LiB additives and LiB electrolytes in one vessel filling with 100 mL Hydranal NEXTGEN Coulomat A-FA and 5 mL Hydranal NEXTGEN Coulomat C FA.[11]

11. For good results, the water recovery of a 100 ppm water standard should be in the range of 90-110%.

TEST METHODOLOGY

Reagents

All tests have been performed with 100 mL 34471 Hydranal NEXTGEN Coulomat A-FA as anolyte and 5 mL 34470 Hydranal NEXTGEN Coulomat C-FA as catholyte.

At the beginning, in between and after each series of titrations, 1 mL of alcohol-free 34446 Hydranal-Water Standard 0.1 PC was titrated to check the recovery and the reliability of results.

The titration tests were performed with sample sizes in a range of 0.5-2 mL. All calculations were done based on differential weighing on analytical balance.

Titration device

All titrations have been performed on Metrohm 852 Titrando titrator with a generator electrode with diaphragm. Prior to the test, all titration cell parts (generator electrode, stirring bar and glass stopper) were dried in the oven at 50°C for 2 h. Drift was stabilized before each titration for 70-100s. Drift correction was turned on. Minimum titration time was 25 s.

TITRATION PARAMETERS	
Polarization current	10 µA
Gen. current	auto
End point	50 mV
Dynamics	70 mV
Max. rate	max. µg/min
Min. rate	15 µg/min
Extraction time (min. titration time)	25 s
Rel. stop drift	5 µg/min
Stirring speed	8
Start drift	20 µg/min
Drift correction	auto
Stop time	off
Stability time	15 s
Pause	0 s

CONCLUSION

The new Hydranal NEXTGEN Coulomat A-FA and C-FA reagents allow the accurate measurement of water content in many different types of electrolytes, as well as in their raw materials, including problematic additives such as VC, FEC and borates.

So far, in standard alcoholic KF reagents, many LiB electrolyte components caused side effects leading to an increase in drift, and delayed or no titration endpoint, rendering incorrect water content results. That could even make water determination impossible.

The new alcohol-free formulation of Hydranal NEXTGEN Coulomat A-FA and C-FA reagents suppresses these side effects and allows for accurate water determination, even in difficult samples. Additionally, the new formulation does not contain CMR (carcinogenic, mutagenic and reprotoxic) substances or halogenated hydrocarbons.

THE HYDRANAL ADVANTAGE: DEDICATED TECHNICAL SUPPORT

With 40 years of experience, Hydranal offers unparalleled global technical support in the field of Karl Fischer titration. Our team of experts is happy to address your questions and can be contacted directly via email at **hydranal@honeywell.com** or at any of our live seminars and webinars.

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