Protocol for Quantifying All Electrolyte Compositions in Aged Lithium-ion Batteries

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The aging of lithium-ion batteries (LIBs) typically accompanies the degradation of electrolyte, but the relationship between them remains unclear. Therefore, quantifying residual electrolyte in batteries at different states of health (SOH) is a crucial issue. Here, we have developed a comprehensive characterization method to quantitatively analyze the electrolyte salts, solvents, and additives in commercial pouch cell, achieving quantification of all electrolyte compositions with high accuracy. Compared to the reported external standard method used in gas chromatography-mass spectrometry (GC-MS), we developed an internal standard method, which offers higher accuracy and reliability, with the maximum error decreased from 9.54% to 3.48%. Moreover, the quantitative accuracy of the calibration curves remains unchanged after 2 months. Multi-instruments analysis is also utilized for the extraction and quantitative analysis of electrolyte in practical battery systems, achieving less than 5% quantification error for all compositions. With our proposed method, it becomes possible to determine the absolute amounts of all electrolyte compositions, rather than obtaining limited information such as concentration or relative content. It is believed that this protocol of quantifying electrolyte compositions in commercial cells could serve as a baseline for further studies to reveal the relationship between electrolyte degradation and battery aging.

Introduction

Since the commercialization of LIBs in 1991, it has been widely used in consumer electronics, electric vehicles and energy storage due to LIBs' high energy density and long cycle life. LIBs typically consist of anode, cathode, separator and nonaqueous liquid electrolyte. The electrolyte plays the role of transporting Li$^+$ between the anode and cathode while separating electronic pathway in between. In most of electrolyte in LIBs, LiPF$_6$ is the most widely used lithium salt, dissolved in a mixture of carbonate solvents. The solvent mixture is typically composed of ethylene carbonate (EC) with a high dielectric constant, combined with low-viscosity linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC).[1] Moreover, various additives, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), are used to further improve the performance of LIBs.

In common LIBs, the electrochemical stability window of the electrolyte (1–4.5 V vs. Li$^+$/Li) is situated beyond the working potential of the graphite anode (0.05 V vs. Li$^+$/Li).[2] Consequently, during the initial charge cycle, the electrolyte undergoes reduction at the graphite anode, forming a solid electrolyte interface (SEI). An ideal SEI should exhibit excellent Li$^+$ conductivity but electronic insulation, thereby preventing further reactions between the electrolyte and the graphite anode.[3,4] However, SEI is often unstable,[3] and the cyclic insertion/extraction of Li$^+$ induces expansion and contraction of the electrode, generating stress that leads to SEI fracture or breakage of active material particles. This results in the exposure of new electrode interfaces, triggering further parasitic reactions of electrolytes.[5,6] Consequently, SEI gradually thickens over repeated charge-discharge cycles, causing continuous consumption of electrolyte and active lithium.[7] The degradation of electrolytes not only occurs at the electrolyte electrode interface but also within the bulk electrolyte phase, such as the thermal decomposition and hydrolysis of LiPF$_6$, transesterification of carbonate solvents,[8,9] and polymerization reactions[3,10,11] that generate oligo carbonates, glycols, oligo phosphates, etc. Electrolyte degradation at the interface and in the bulk phase both lead to a decrease in battery dynamic performance.[12] Furthermore, the sudden decay in battery capacity has been confirmed to be related to the depletion of electrolyte additives.[13,14] When electrolyte is continuously consumed to a certain point (e.g. the volume of the electrolyte is smaller than that of the pore within the electrode, namely the electrolyte drying-out), it may lead to capacity diving, resulting in battery failure.[15] Therefore, clarifying the residual electrolyte

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at different SOH is crucial for revealing the mechanism of battery degradation and failure.

The growth of SEI is commonly regarded as the main cause of battery aging,[16,17] but the current understanding of SEI remains insufficient, and characterization techniques such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) could only provide localized and qualitative information. To obtain more SEI information, one crucial path is to quantify residual electrolyte. Zhou et al.[18] determined the electron transfer number for the formation of SEI by quantifying residual electrolyte, thus deciphering the main electrolyte decomposition mechanism and obtaining the main composition information of SEI, which overcame the limitations of traditional SEI characterization methods.

The development of quantitative methods for residual electrolyte plays a crucial role in elucidating the mechanisms of battery aging and failure. For the quantification of residual electrolyte, the first and most important thing is to extract the electrolyte from cells, typically achieved through centrifugation,[19–21] liquid-liquid extraction,[22] and injection of diluents.[23–25] However, due to the inability to completely extract the electrolyte from cells, most studies only provide information on the concentration or the relative content of electrolyte compositions. Due to simultaneous decrease in both the total amount of electrolyte and the amount of compositions during battery aging, the concentration of most compositions tends to remain unchanged. Only compositions with significant decomposition, such as additives, exhibit a decreasing trend of concentration. Therefore, the change of electrolyte concentration can only provide limited information. Additionally, current research on electrolyte quantification mainly focuses on a single category of compositions (solvents or lithium salts). However, the consumption of electrolyte compositions may interact with each other, and all of them will lead to battery degradation. Hence, obtaining information on the residual amounts of all electrolyte compositions holds greater practical significance.

Here, we report a method that can extract the electrolyte from batteries completely in a facile manner. We then accurately quantified the absolute amounts of all compositions in the electrolyte through a combined analysis of gas chromatography-mass spectrometry (GC-MS), nuclear magnetic resonance (NMR), and inductively coupled plasma optical emission spectrometry (ICP-OES), with a maximum quantification error of $< 5\%$. Furthermore, we developed an internal standard method rather than external standard for GC-MS measurement, allowing the accurate quantification of solvents and additives in the electrolyte even after establishing the calibration curve 2 months later. Moreover, both the extraction and quantification method are highly reproducible with small measurement deviation.

Experimental Details

Chemicals and Electrolytes

Battery-grade DMC, EMC, EC and VC were purchased from Canrd (Guangdong, China). DEC (purity: 99.9%) was obtained from Ningde Kaixin (Ningde, China) for battery immersion. HPLC-grade dichloromethane was purchased from Acemec (Shanghai, China). GC-MS internal standard 1,1,3,3-tetramethylurea (purity: 99%) from Energy chemical (Shanghai, China) was used. NMR internal standard 1,4-bis(trifluoromethyl)benzene (purity: 99%) from Aladdin (Shanghai, China) was used. NMR internal standard benzylsulfonyl fluoride (purity: 99%) from Boer was used. The electrolytes used in the experiments are shown in Table 1.

Cells

Pre-packaged 110 mAh LiFePO$_4$/graphite pouch dry cells (without electrolyte) were provided by Contemporary Amperex Technology Co., Ltd. The dry cells mainly consist of a layer of graphite anode (43.5×51 mm) coated on both sides, two layers of separators, and two layers of LiFePO$_4$ cathode (42×49.5 mm) coated on single side, and the capacity ratio of negative to positive is 1.1. 500 μL commercial electrolyte E3 was injected into dry cell in a glove box filled with argon (H$_2$O < 0.01 ppm, O$_2$ < 0.01 ppm), and then vacuum-sealed at a gauge pressure of −95 kPa. The vacuum-sealed dry cells were placed at 25 °C for over 48 hours, so as to allow the free electrolyte diffusing into anode, cathode and separator to reach a fully wetted state. This calendaring process serves as a vanilla version of aged battery where the electrolyte is fully adsorbed and partially reacted, and we focus on those physically adsorbed and unreacted electrolyte in the battery system in this study. The actual amount of electrolyte injected into the fresh cells is obtained from the difference in mass before and after electrolyte injection, so the fresh cells with known amount of electrolyte were used for verifying the accuracy of electrolyte quantification.

Electrolyte Extraction by Centrifugation

As illustrated in Figure S1, the pouch cells were cut open along one side, then rolled into the centrifuge tube with the cut side facing down allowing electrolyte to be separated from the battery. The centrifuge tube was then placed in a centrifuge machine and centrifuged at a speed of 5000 rpm for 20 minutes to extract the electrolyte from the battery (Figure S1(c)).

Electrolyte Extraction by Injection of Diluent

The pouch cell was cut open and 500 μL of diluent (a substance not contained in the electrolyte) was injected, then it was heat-sealed and left for 8 days allowing thorough mixing of the diluent with the electrolyte.[21,23] After thorough mixing, the battery was cut open again, and the mixture of diluent and electrolyte was extracted from the cell by squeezing or centrifugation.

Table 1. Electrolytes used in experiments.

Electrolytes	Compositions
E1	1 mol/ LiPF$_6$ in DMC:EMC:EC=1:1:1 wt%, with 1 wt% VC
E2	1 mol/L LiFSI in DMC:EC=1:1:1 Vol%
E3	0.7 mol/L LiPF$_6$ and 0.3 mol/L LiFSI in EMC:DMC:EC=1:2.3:3 wt%, with 2 wt% VC

As show in Equations (1) and (2), this method can be used to obtain the absolute amount of electrolyte and its compositions by knowing the amount of injected DEC.[23,25]

$$m_{electrolyte,cell} = \frac{m_{DEC,inject}}{m_{DEC,extract}} - m_{DEC,inject} \qquad (1)$$

$$n_{component,cell} = \frac{m_{DEC,inject}}{w_{DEC,extract}} \cdot c_{component,extract} \qquad (2)$$

where $m_{electrolyte,cell}$ is the mass of the original electrolyte in the cell, $m_{DEC,jinject}$ is the mass of the injected DEC, $w_{DEC,extract}$ is the quantified mass fraction of DEC in the extract; $n_{component,cell}$ is the amounts of the component to be determined in the cell, and $c_{component,extract}$ is the quantified concentrations (with a unit of mol/g) of the component in the extract.

Electrolyte Extraction by Immersion

The process is shown in Figure 1. The entire process was carried out in a dry room (dew point $-78\,°C$) to prevent hydrolysis of LiPF$_6$. Firstly, the cell was cut into 4 pieces and placed into a
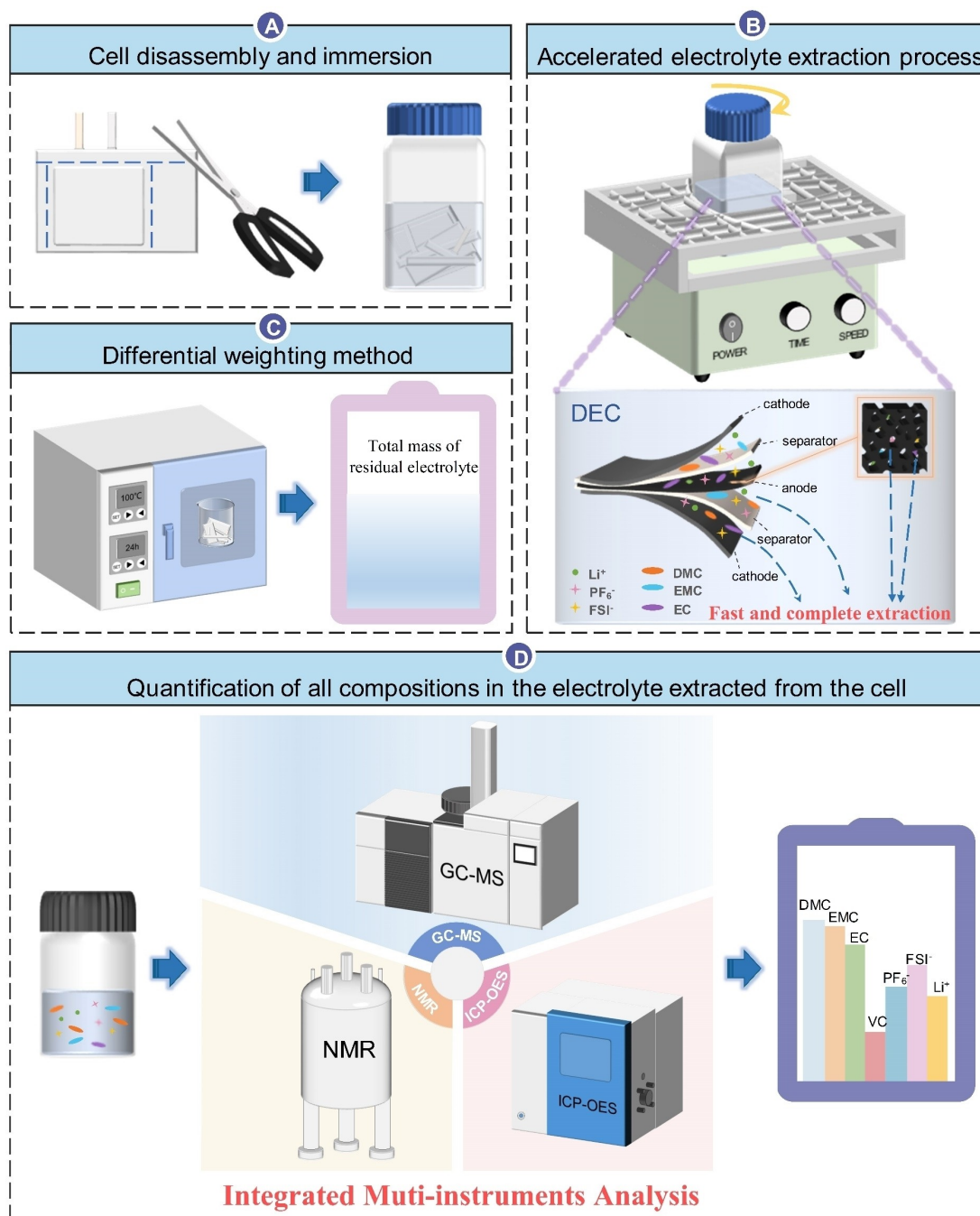

Figure 1. Schematic diagram of extracting electrolyte from batteries using the DEC immersion method, and the quantification of all compositions in the electrolyte.

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polytetrafluoroethylene (PTFE) bottle containing ~70 ml of immersion solvent. The immersion solvent covered the battery components, facilitating the dissolution of electrolyte from the cell in the immersion solvent. Since the immersion solvent is not battery-grade, it may contain some moisture leading to the hydrolysis of $LiPF_6$. As shown in the Figure S2, after leaving the immersion solution for more than a day, most of the $LiPF_6$ hydrolyzed and its hydrolysis product POF_nR_{3-n}[26] was detected. Therefore, in order to extract the electrolyte from the cell quickly and completely, the PTFE bottle containing the immersed cell was placed on an oscillator and shaken for 1 hour to accelerate the exchange process between the immersion solvent and the electrolyte inside the cell. After immersion, the cell components and the immersion solution were separated, and was subjected to further process to quantify the total mass of the electrolyte and the amount of all compositions in the electrolyte. The further treatment of the immersion solution into samples for GC-MS, NMR, and ICP-OES analysis, as well as the instrumental testing conditions, can be found in the Supporting Information.

The absolute amount of electrolyte composition x in the cell is calculated as shown in Equation (3) and Figure S3. Documenting the dilution ratio during sample preparation enables us to determine the absolute amount of all electrolyte compositions in the cell using the equation below:

$$n_x = \frac{w_x m_3}{M_x} \times \frac{m_1}{m_2} \tag{3}$$

where w_x is the mass fraction of composition x obtained by GC-MS with internal standard method, M_x is the relative molecular mass of composition x, m_1 is the mass of added DEC (~70 mL), m_2 is the mass of immersed DEC solution used for further analysis (~2 mL), m_3 is the mass of diluted immersed DEC solution with added dichloromethane (~20 mL). Note that DEC generated by transesterification side reaction has no effect on the quantitative accuracy of this method.

The calculation process for the absolute amount of lithium salt in the cell quantified by NMR and ICP-OES is similar, where w_x is determined by NMR or ICP-OES.

Results and Discussion

Electrolyte Extraction

Quantitative analysis of electrolyte requires its extraction from the cell. Currently there are mainly three methods: centrifugation, injection of diluent, and immersion, and they have been summarized in Table 2. Due to the difficulty in extracting electrolyte from the pores of electrodes and separators, centrifugation can only extract about half of the electrolyte in the cell as shown in Table S3, thus it can only provide the concentration or relative content of compositions but not the absolute amount and it is not suitable for batteries after long-cycles.

The methods of injecting diluent and immersion both require the introduction of a new solvent, which should dissolve all compositions in the electrolyte, and not react with any components in the battery. As far as we know, the solvents commonly used for electrolyte extraction include dichloromethane (DCM), trichloromethane (TCM), acetonitrile (ACN), and dimethyl sulfoxide (DMSO). However, these solvents cannot simultaneously satisfy the above two requirements. DCM and TCM were used as the extraction solvent to acquire only the soluble organic components of the electrolyte but not the insoluble lithium salts, while ACN and DMSO react with battery components. Acetonitrile reacts with lithium metal and therefore it can only be used for electrolyte analysis of batteries without lithium plating. And electrolyte discoloration is observed in the presence of DMSO possibly due to side reactions. A carbonate-based solvent not contained in the electrolyte could meet these requirements, and here we use DEC as the diluent solvent, which is absent in electrolyte E3. Electrolyte extraction for other batteries can refer to this method and choose a solvent that is commonly used in electrolytes but not a part of them.

Injecting DEC into cell is followed by squeezing the mixed solution of DEC and electrolyte similar as centrifugation, which cannot completely extract the electrolyte from the battery.

Table 2. Summary of electrolyte extraction methods.

Electrolyte Extraction Methods	Immersion Solvent/diluent	Reference	Available Information	Limitations
Centrifugation	/	[19–21,27]	Relative content of all electrolyte compositions	Low extraction rate (not suitable for batteries after long-cycles)
Immersion	DCM, TCM	[21,22,28]	Absolute amount of electrolyte solvents and additive	Unable to quantify lithium salts
	DMSO	[28]	/	Reacts with battery components, causing discoloration of the electrolyte
	DEC	This work	Absolute amount of all electrolyte compositions	/
Injection of Diluent	DEC	[23,25]	Absolute amount of all electrolyte compositions	(1) Quantification accuracy is affected by the transesterification byproducts DEC; (2) The procedure requires extreme caution to prevent any loss of DEC
	ACN	[24,29,30]	Relative content of all electrolyte compositions	The diluent reacts with lithium metal, making it applicable only for batteries without lithium plating

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However, unlike the centrifugation method, this method allows us to calculate the absolute amount of electrolyte by knowing the injected amount of DEC, as described in Section 2.4. Note that the process of injecting DEC and resealing the battery must be performed with great care, otherwise any loss of DEC will affect the quantification accuracy as shown in Table S4. Moreover, the transesterification side reactions in the electrolyte may generate new DEC, leading to an increase in $w_{DEC,extract}$, thus affecting the quantification accuracy. Furthermore, this method requires 8 days to thoroughly mix the diluent and electrolyte, resulting in a long experimental period.

The immersion method also uses DEC as the immersion solvent, and its procedure is shown in Figure 1 and detailed in Section 2.5. Since DEC is capable of dissolving all electrolyte compositions, theoretically sufficient immersion could dissolve all the electrolyte in the battery into the immersion solvent. Therefore, the absolute amount of electrolyte compositions in the battery can be directly calculated by converting the concentrations obtained from instrumental analysis through the dilution process (Section 2.5). And as shown in Equation (3), since the quantification in the immersion method is independent of w_{DEC}, the accuracy of this method is not affected by the generation of DEC from transesterification side reactions. The ability of the DEC immersion method to completely extract the electrolyte from the battery is verified in Section 3.3.

Calibration of Multi-Instrument Analysis

Quantification of Solvents and Additives by GC-MS

Solvents and additives are typically analyzed using GC-MS, which provides good separation of each composition (Figure 2(a)). In chromatography, different substances have different response factors, so concentrations cannot be directly compared based on peak height or area.[31] It is necessary to establish a relationship between concentration and response intensity via a calibration curve to determine the unknown concentration of sample solutions, i.e. the external standard method. The calibration curves of electrolyte solvents and additive are shown in Figure S5, and all the calibration curves have a good linear correlation, with R^2 greater than 0.996. Furthermore, electrolyte E1 with a known formulation was diluted with dichloromethane to concentrations within the range of calibration curves, and then GC-MS tests were carried out to get the concentration of each composition in electrolyte E1, and the quantification error was calculated by comparing it with the actual concentration. The results are shown in Table 3, except for DMC, which is highly volatile that affects its quantification, the quantitative errors for other compositions are all less than 5%. However, after the establishment of calibration curves for 2 months, the accuracy was re-validated using the same electrolyte E1 and the quantitative errors for all compositions surged to about 50%. This is mainly due to the gradual change in instrument status, resulting in significant
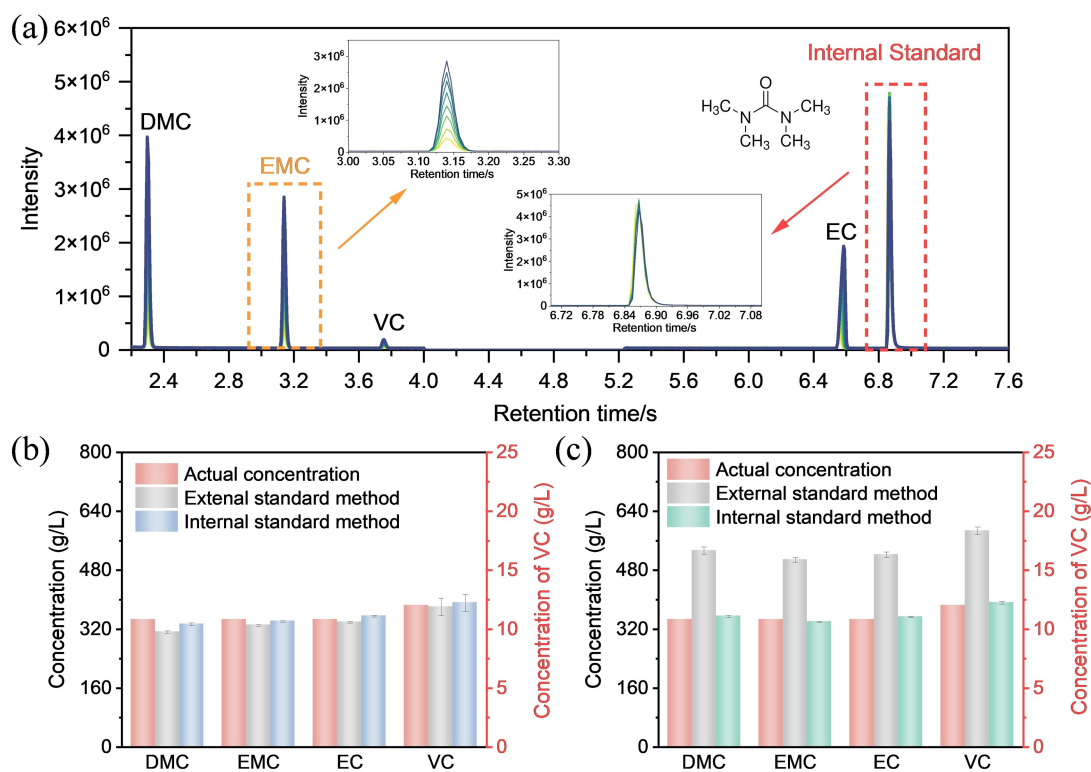

Figure 2. Total ion chromatogram (TIC) graph of the standard solutions with 8 gradients (see Table S1 for details) (a). Comparison of measurement accuracy between internal standard method and external standard method using the calibration curves immediately (b), or after 2 months (c). Refer to Table 3 and Table 4 for details, with error bars indicating deviations from three separate tests.

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Table 3. Accuracy variations in external standard method (validated by electrolyte E1 with a known formula).

Compositions	Actual Concentration (g/L)	Immediate Validation		Validation After 2 Months	
		Concentration (g/L)	Error (%)	Concentration (g/L)	Error (%)
DMC	345.36	312.41	−9.54	533.2	54.38
EMC	345.36	330.73	−4.24	508.6	47.26
EC	345.36	339.18	−1.79	522.0	51.14
VC	12.00	11.89	−0.90	18.3	52.82

differences in response intensity for the same substance at the same concentration after a period of time (Table S5), making the concentration-intensity relationship of the calibration curve only applicable for short-term analysis, indicating the short timeliness of the calibration curve.

The problem of calibration curve failure can be solved through the internal standard method. Adding internal standard to both the standard and sample solutions and keeping the concentration of the internal standard constant, and establishing a relationship between relative concentration (w_x/w_{st}) and relative response intensity (I_x/I_{st}), instrument drift can be corrected and the timeliness of the calibration curve can be extended.

The internal standard typically needs the following requirements: (1) it does not react with any compositions in the electrolyte and can exist stably; (2) it can be completely dissolved in the sample solution; (3) it is similar in nature to the analyte and the retention time is close but does not overlap with others, ensuring that any slight changes in instrument status have similar effects on both the analyte and internal standard. Here, the additive 1,1,3,3-tetramethylurea, which is less commonly used in electrolyte of LIBs, was used as the internal standard. It exhibits good compatibility with the electrolyte and the retention time is similar to the electrolyte compositions (Figure 2(a)). The calibration curves established by adding 1,1,3,3-tetramethylurea are shown in Figure S6, and the linear correlation coefficients R^2 of all calibration curves are greater than 0.998, which is better than the external standard method. And as shown in Table 4, the quantitative accuracy of each composition was greatly improved, with the maximum error decreased from 9.54% to 3.48%. Furthermore, due to the use of relative response intensity (I_x/I_{st}) by internal standard method, which does not vary with instrument status (Table S5),

the quantitative accuracy remained nearly unchanged after 2 months, greatly extending the timeliness of the calibration curve as show in Figure 2(c) and Table 4.

Quantification of Lithium Salts by NMR and ICP-OES

Due to the inability of lithium salts to be vaporized in GC, GC-MS cannot be used for the analysis of lithium salts, instead, ion chromatography (IC), NMR, and ICP-OES are usually used for this purpose. In solution NMR, the peak area is directly proportional to the number of corresponding atoms in the substance, therefore, as shown in the Equation (4), the NMR internal standard method can be used to calculate the amount of the analyte by adding a known amount of internal standard, without the need to establish calibration curve, which is more convenient and efficient. Therefore, the lithium salts in electrolyte E3, including PF_6^- and FSI^-, were quantified using NMR internal standard method. Internal standards generally have the following requirements: 1) Chemical inertness, not reacting with any substance in the sample solution; 2) Solubility in the solvent used; 3) Chemical shift close to the analyte but not overlapping. Based on the above requirements, as shown in Figure 3(a,b), 1,4-bis(trifluoromethyl)benzene with a chemical shift of 63.97 ppm was used as the internal standard for PF_6^- quantification,[24] and benzylsulfonyl fluoride with a chemical shift of 49.85 ppm was selected as the internal standard for FSI^- quantification. The ^{19}F NMR spectra of these two internal standards are simple, with only one peak, and both are close to the peaks of the analytes. The quantitative accuracy of these two internal standards was verified using known formula of electrolyte E1 and E2. After diluting the electrolyte with DEC and adding an appropriate amount of internal standard, the

Table 4. Accuracy variations in internal standard method (validated by electrolyte E1 with a known formula).

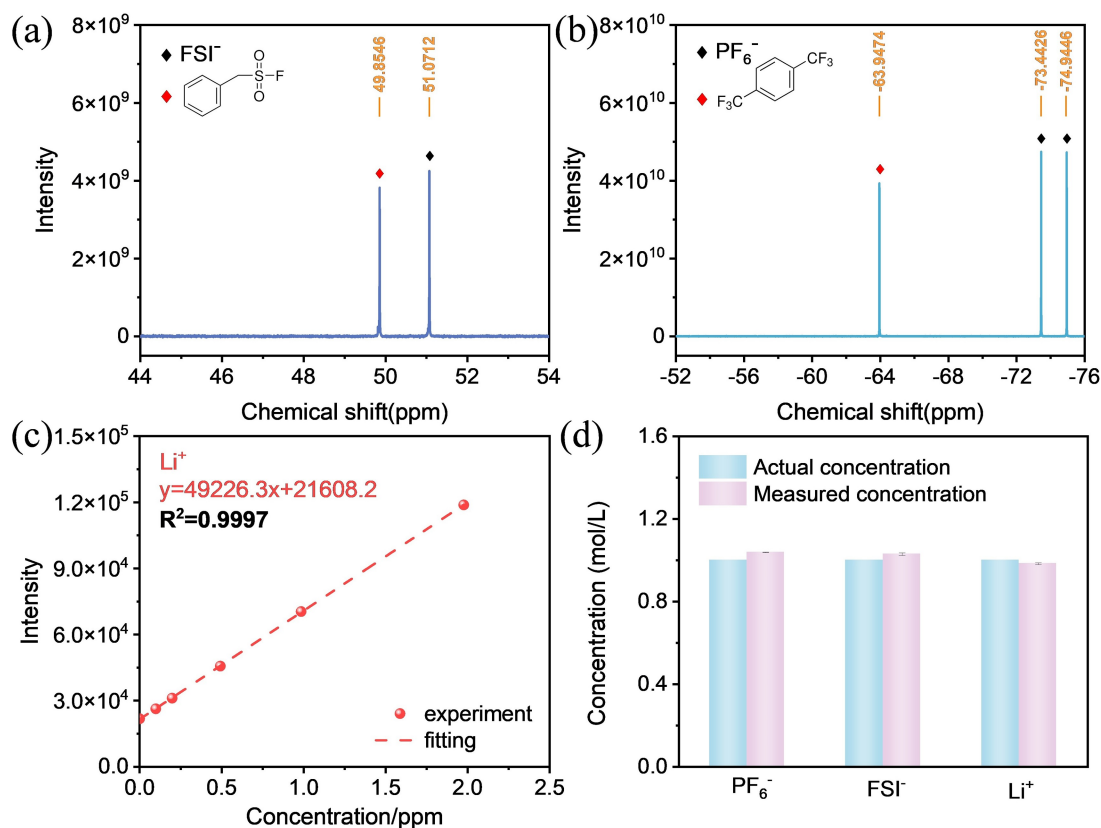| Compositions	Actual Concentration (g/L)	Immediate Validation		Validation After 2 Months	
		Concentration (g/L)	Error (%)	Concentration (g/L)	Error (%)
DMC	345.36	333.34	−3.48	355.2	2.86
EMC	345.36	341.30	−1.18	340.3	−1.46
EC	345.36	355.37	2.90	352.9	2.17
VC	12.00	12.23	1.91	12.2	2.08

Figure 3. (a) ^{19}F NMR spectra of FSI$^-$ and benzylsulfonyl fluoride internal standard (b) ^{19}F NMR spectra of PF$_6^-$ and 1,4-Bis(trifluoromethyl)benzene internal standard (c) Calibration curve of Li$^+$ established by ICP-OES (d) Quantitative accuracy of PF$_6^-$, FSI$^-$, and Li$^+$ (the accuracy of PF$_6^-$ and Li$^+$ was validated using electrolyte E1, and the accuracy of FSI$^-$ was validated using electrolyte E2, see Table S6 for details, and error bars indicate deviations from three tests).

solution was transferred to NMR tubes for testing. The concentration of lithium salts in the electrolyte was calculated, and quantitative errors were determined by comparing with actual concentrations. As shown in Table S6 and Figure 3(d), the quantification errors for PF$_6^-$ and FSI$^-$ were 3.78% and 2.98%, respectively, both of which were highly accurate. The Li$^+$ in the electrolyte was quantified using ICP-OES to establish the relationship between Li$^+$ concentration and response intensity (Figure 3(c)). The validation results of electrolyte E1 showed that Li$^+$ was quantified with an error of 1.67%.

$$m_x = \frac{M_x}{M_{st}} \times \frac{A_x}{A_{st}} \times \frac{N_{st}}{N_x} \times m_{st} \times P \tag{4}$$

where x is PF$_6^-$ or FSI$^-$, st is the corresponding internal standard, m the mass, M the relative molecular mass, A the peak area in NMR, N the number of fluorine atoms contained in the substance, and P the purity of the internal standard, which is 99%.

Application of DEC Immersion Method and Electrolyte Quantification Methods in Practical Batteries

To simulate the extraction and quantification of electrolyte from aged batteries, we used three fresh parallel cells with known amount of electrolyte, which were completely wetted, and the process is shown in Figure 1, see Section 2.5 for details. After immersion, the cell components and the immersion solution were separated.

The amount of electrolyte solvents and additives in the cell can be obtained by analyzing the DEC immersion solution using the established GC-MS internal standard method. However, due to the large amount of DEC in the immersion solution, direct testing not only damages the ion source of MS but also completely destroy the peaks of the preceding compositions (DMC, EMC, VC), as shown in Figure 4(a), making it impossible for quantitative analysis. Therefore, it is necessary to dilute the DEC immersion solution with low-boiling-point dichloromethane (retention time < 2 min) to reduce the proportion of DEC before the GC-MS test. As shown in Figure 4, when diluted to a DEC proportion of < 10%, except for VC being dispersed into two peaks (the response intensity of VC is the sum of the two peaks), all other compositions exhibit normal peaks. Considering that excessive dilution may affect the quantification of compositions with lower content in the electrolyte (such as additives), the optimal proportion of DEC is determined to be 10%. As shown in Figure S3, after diluting the immersion solution with dichloromethane to about 10% DEC, internal standards were added, and GC-MS test was performed. The quantitative results for the solvents and additives are shown in Table 5, which are consistent with the actual injected amount,
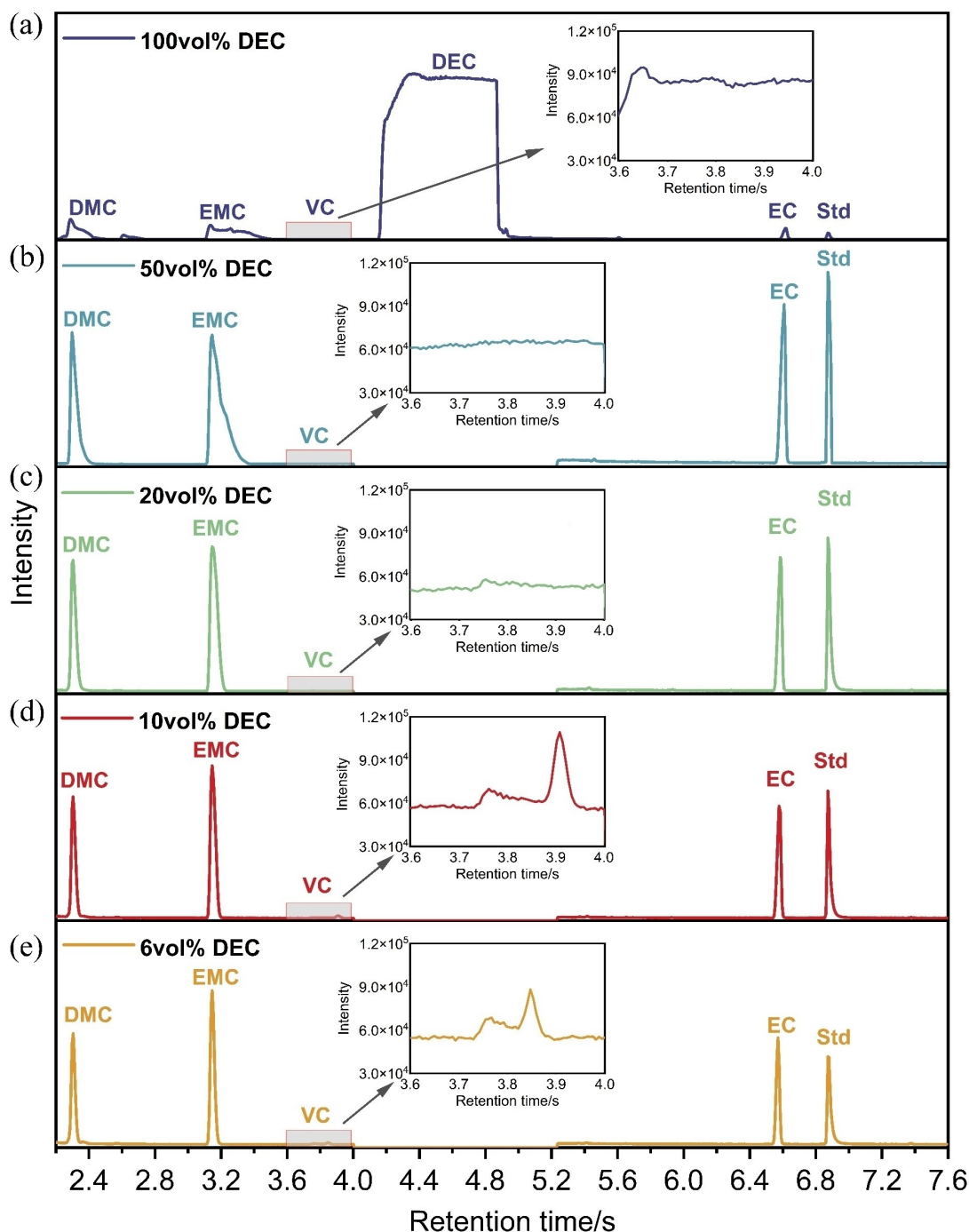
Figure 4. TIC graph of GC-MS samples (Dilution of DEC immersion solution with dichloromethane results in different proportions of DEC in the solution).

with a maximum error of 4.4%. Moreover, the quantification results of the three separate cells all demonstrated high accuracy, indicating the high reproducibility of this method.

The amount of lithium salts in the cell can be obtained by analyzing the DEC immersion solution using ICP-OES and the NMR internal standard method. Since ICP-OES requires the sample to be an aqueous/weak acid solution, but the immersion solution is dominated by the DEC organic solvent. Thus it is necessary to digest the organic components (electrolyte solvent and DEC) in immersion solution with concentrated

nitric acid and hydrogen peroxide. As shown in Figure S7, when organic components begin to be oxidized and digested, nitric acid is simultaneously reduced to generate NO_2 (brown-red smoke). With the continuous oxidation of organic components and the dissipation of NO_2, the solution gradually lightens in color and eventually becomes clear and transparent again, indicating that the organic components in the solution have been completely digested. After digestion, the sample was diluted with deionized water to a Li^+ concentration of ppm and subjected to ICP-OES test. The quantification results are shown

Table 5. Quantitative accuracy of all electrolyte compositions extracted from the cells using the DEC immersion method (the unit for injected amount and extracted amount is μmol).

Compositions	Injected Amount	Quantification Methods	Fresh Cell 1		Fresh Cell 2		Fresh Cell 3	
			Extracted Amount	Error (%)	Extracted Amount	Error (%)	Extracted Amount	Error (%)
DMC	2762.7	GC-MS	2826.1	2.3	2848.6	3.1	2846.9	3.1
EMC	775.7		803.8	3.6	810.2	4.4	802.9	3.5
EC	2089.2		2078.5	−0.5	2064.1	−1.2	2052.4	−1.8
VC	136.4		135.8	−0.4	136.4	0.0	134.8	−1.2
PF_6^-	366.4	NMR	363.7	−0.7	355.3	−3.0	358.9	−2.1
FSI^-	154.6		150.9	−2.4	162.5	5.1	160.3	3.7
Li^+	516.9	ICP-OES	506.6	−2.0	508.0	−1.7	517.2	0.1

in Table 5, which are consistent with the actual injected amount, with a maximum error < 2.0%. Moreover, the quantification results of three cells are all highly accurate, indicating that the extraction of electrolyte and the Li^+ quantification method are highly reproducible and accurate, and the digestion process of organic matter does not alter Li^+ concentration. The amount of lithium salt anions PF_6^- and FSI^- in the immersion solution is determined by the NMR internal standard method, as shown in Table 5, both of which are consistent with the actual injected amount.

The total mass of the electrolyte is obtained by drying the components of the cell after immersion, which is performed in the dry room. The cell components are placed in a 100 °C oven for more than 24 hours, then, the total mass of electrolyte can be obtained by subtracting the mass of cell components after

drying from the mass before cell disassembly (differential weight method). As shown in Table 6 and Figure 5, the total mass of the electrolyte obtained from three parallel fresh cells by differential weight method is basically consistent with the actual injected amount, with errors all less than 1%. Each composition quantified through multi-instrument analysis is summarized in Table 5. Both the differential weigh method and the multi-instruments analysis prove to be accurate methods to quantity the injected electrolyte in the pouch cell after aging, with multi-instruments analysis giving more details on the accurate amount of each species.

The results of electrolyte extraction and quantification on fresh cells showed that the DEC immersion method can completely extract the electrolyte from the cell, and the extraction process can be accelerated by shaking on an

Table 6. Accuracy of quantifying the total mass of electrolyte using the differential weight method for three parallel cells.

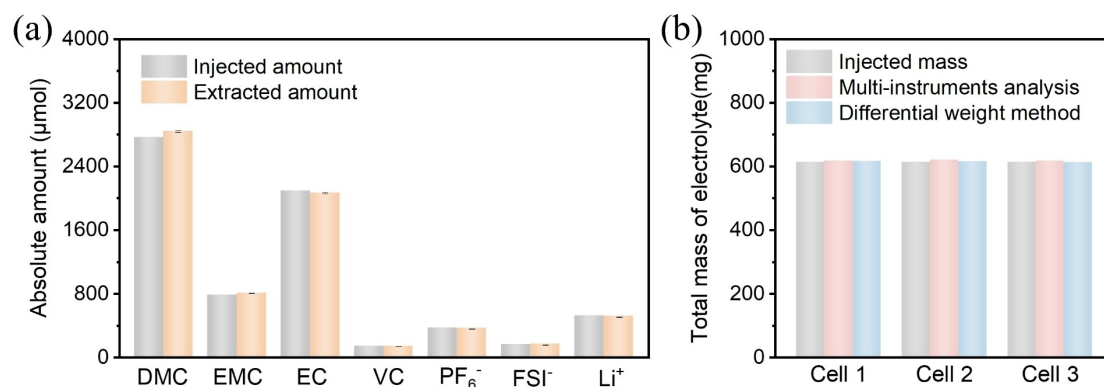| Cells	Injected Mass (mg)	Differential Weight Method		Multi-instruments Analysis	
		Extracted mass (mg)	Error (%)	Extracted mass (mg)	Error (%)
Fresh cell 1	612.9	615.6	0.44	616.4	0.57
Fresh cell 2	612.5	614.0	0.24	618.7	1.01
Fresh cell 3	613.0	611.5	−0.24	616.9	0.64

Figure 5. (a) Accuracy of quantifying all electrolyte compositions in the cell (see Table 5 for details, and error bars indicate the deviation among three parallel cells); (b) Accuracy of quantifying the total mass of electrolyte by differential weight method (validated by three fresh cells, see Table 6 for details).

oscillator. The immersion solution was analyzed by integrated multi-instrument analysis of GC-MS, NMR, and ICP-OES to quantify the absolute amount of all electrolyte compositions with high accuracy, yielding a maximum error about 5 % (Table 5 and Figure 5(a)). And the total mass of electrolyte can be accurately quantified by differential weight method, with a maximum error about 0.5 % (Table 6 and Figure 5(b)). Additionally, consistent high quantification accuracy is achieved for three separate cells, indicating that the entire method is highly reproducible. The fact that extracted electrolyte agrees well with the injected electrolyte also indicates that physical aging of the battery without electrochemistry cycling under the condition in this study do not consume or trap substantial electrolyte.

Conclusions

This work proposes a comprehensive method capable of extracting residual electrolyte from pouch cells completely and allowing the accurate quantification of the absolute amount of all electrolyte compositions through multi-instruments analysis including GC-MS, NMR, and ICP-OES, with a maximum error less than 5 %. Notably, we developed the immersion extraction method which is proven to be able to fully extract residual electrolyte, and we reported the internal standard method for GC-MS that can extend the calibration life for longer time period. Moreover, the entire method shows consistent high accuracy in three parallel cells, indicating that the method is highly reproducible. The reported method in this study here, though used to quantify the electrolyte in small-sized pouch LIBs, can be easily extended to quantify the electrolyte in other batteries format with appropriate adjustments. For example, in large batteries of Ah level, it is necessary to increase the amount of immersion solvent and extend the immersion time to ensure that all the electrolyte components in the battery are dissolved. It is hoped that this method would serve as a benchmark study for future quantification of battery electrolyte and electrolyte decomposition in various application scenarios. Based on this study, future development of in-situ analysis techniques such as in-situ spectroscopy could potentially capture of reaction intermediates so as to study the electrolyte degradation mechanisms,[32–36] accelerating our understanding of the relationship between electrolyte decomposition and battery aging.

Conflict of Interests

The authors declare no competing financial interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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