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J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.6b12970 • Publication Date (Web): 13 Feb 2017

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Purification and Characterization of Reclaimed Electrolytes from Spent Lithium-Ion Batteries

Yuanlong Liu‡, Deying Mu‡, Ruhong Li†, Quanxin Ma†, Rujuan Zheng† and Changsong Dai‡,*

1MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, P.R. China.

2Department of Environmental Engineering, Harbin University of Commerce, Harbin 150076, P. R. China.

3State Key Laboratory of Advanced Chemical Power Sources, Zunyi, 563003, P. R. China.

‡These authors contributed equally.

*Corresponding author: Changsong Dai

Tel: +86-451-86413751, Fax: +86-451- 86418616, E-mail: changsd@hit.edu.cn
Abstract

As an indispensable part of lithium-ion batteries (LIBs) closed-loop recycling, reusing the electrolyte from spent LIBs has not yet been fulfilled experimentally. Herein, this paper presents a LIB electrolyte recycling approach which consists of supercritical CO$_2$ extraction, resin and molecular sieve purification and components supplement. The resultant electrolyte exhibited a high ionic conductivity of 0.19 mS·cm$^{-1}$ at 20 °C, which was very close to commercial electrolyte with the same composition. Moreover, the electrolyte was also electrochemically stable up to 5.4 V (vs. Li/Li$^+$) in the linear sweep voltammetry (LSV) measurement. The application potential of reclaimed electrolyte was demonstrated by Li/LiCoO$_2$ battery presenting the initial discharge capacity of 115 mAh·g$^{-1}$ with a capacity retention of 66 % after 100 cycles at 0.2 C. This investigation is a crucial break for electrolyte recycling and opens a bright route towards realizing closed-loop LIBs recycling.

1 Introduction

Due to the high voltage, high energy density and good cycling stability, LIBs have been widely used in recent years as an important energy storage and conversion devices to power portable electronic devices and even electric vehicles.$^{1-3}$ It is predicted that, in future years, the amount of waste LIBs will increase with the market expansion and productivity growth of LIBs. The LIBs contain many valuable compositions, thus many of recycling methods emerge as required. In the present scenario, industrial scale reclamation of spent LIBs are based on pyrometallurgical and hydrometallurgical processing.$^{4-6}$ These methods mainly recover valuable metals, while neglecting the recovery of electrolyte.$^{7-9}$ Solutions of lithium hexafluorophosphate (LiPF$_6$) in aprotic organic solvents are widely used as electrolytes in LIBs.$^{10}$ The decomposition products of
electrolyte during recycling may bring inflammable and toxic elements or compounds.11-13 Some of them are considered as nerve agents with comparable toxicity to diisopropyl fluorophosphate,14-16 which is homologue of sarin.17 From the environmental point of view, how to safely dispose the electrolyte items is a crucial and necessary research field.

Recycling of toxic and harmful electrolyte is important, but high recycling cost will be bound to greatly reduce the practical value of the method. Extraction is one of the most effective separation methods for the recovery of electrolytes from the spent LIBs.18, 19 Several organic solvents as extracting agents were examined.20-22 But in comparison with organic solvent extraction, extraction with supercritical carbon dioxide can avoid solvent impurities introduced in electrolyte, and can simplify purification process of extraction product.23 But most important of all, supercritical operations of carbon dioxide are relatively moderate to heat sensitive substances (LiPF₆) in extract or raffinate phase.24-26 Literature search shows several laboratory scale studied on separation and fractionation of carbonate-based electrolyte from spent LIBs by the systems of liquid/supercritical carbon dioxide. The proof of principle experiments for extraction of LIB electrolytes were confirmed by using supercritical helium head pressure carbon dioxide.27 The extraction conditions were optimized with Box-Behnken design.28 Extraction efficiency was enhanced by employing several modifiers.29

The electrolytes reusing is the final and also the most important step of closed loop LIB recycling (Closed loop recycling is basically a production process in which post-consumer waste is collected, recycled and used to make new products.). However, overview of these processes, reusing of electrolytes that recovered by supercritical carbon dioxide extraction has never been reported in literature yet. It is believed that the reusing of electrolytes recovered by supercritical carbon dioxide extraction is possible, because the electrolytes do not differ significantly after
Furthermore, it is well known that there are some differences on the compositions of electrolytes produced in different manufacturers but their major ingredients are similar. And in actual experiment can only evaluates limited major ingredients of electrolyte and their performances under the conventional conditions due to large numbers of electrolyte formula. Therefore in this study, focuses were made on reusing possibility of electrolytes that recovered by supercritical carbon dioxide extraction. We developed a reclamation procedure and investigated operating performance of the reclaimed electrolytes that include ionic conductivity and electrochemical stability. Finally, we compared Li/LiCoO$_2$ battery performances using reclaimed and commercial electrolytes with the same formula.

2. Materials and Methods

2.1 Materials

The spent LIBs are quality control samples of 40 Ah NMC prismatic cells from Harbin Coslight Power Co., Ltd. A series of performance tests were conducted on these samples before being scrapped. A commercially available battery electrolyte (TC-E216#), battery grade carbonate solvents and LiPF$_6$ were purchased from Tinci Materials Technology Co., Ltd. (Guangzhou, China), and used without further purification. The electrolyte consists of 1 M LiPF$_6$ dissolved in EC, EMC and DEC at a mass ratio of 1:1:1. The content of water was < 20 ppm and hydrofluoric acid was < 30 ppm.

2.2 Supercritical CO$_2$ extraction procedure

The free-state electrolyte is few in spent LIBs, and a majority of electrolyte which could not be collected by tipping out is adsorbed in separator and active material. The electrolyte was separated by supercritical carbon dioxide extraction from spent LIB. For each extraction
experiment, discharged batteries were dismantled and enclosed into the extraction vessel in an argon filled glove box with moisture and oxygen level less than 1 ppm. The extraction vessel was transferred to a supercritical CO$_2$ extraction system for electrolyte extraction. After connecting the extraction vessel to the extraction system and adjusting pressure and temperature to extraction conditions (40 °C and 15 MPa), the experiment begun with a static extraction step which was hold for 10 min, followed by 20 min of dynamic extraction with a constant flow rate of 2.0 L·min$^{-1}$. The extracts were cryogenically trapped into a sample flask. The collected sample was tightly sealed and stored in the glove box before analysis. An extraction yield of about 85% could be achieved.

### 2.3 Preparation of Electrolytes

Since the sensitivity of the electrolyte properties to hydrofluoric acid and water content, the extracts were deacidified with Amberlite IRA-67 weakly basic anion exchange resin (Sigma-Aldrich) and dehydrated with activated 4Å lithium substituted molecular sieve.$^{31, 32}$ The anion exchange resin was dried in vacuo at 80 °C for 4 hours, and then contacted with the extracts for 24 hours to remove hydrofluoric acid. Afterward, the extracts were decanted into an airtight container full of activated 4Å lithium substituted molecular sieve for 12 hours. After filtration, the extracts were tightly sealed and stored in the glove box before analysis. These processes were carried out in the glove-box under argon atmosphere. The color contrast of electrolyte in various stages is shown in Fig. S1. The reclamation procedure of electrolyte is illustrated in Scheme 1.

The concentration of the hydrofluoric acid was determined by potentiometric titration with 0.01M potassium hydroxide solution in ethanol, and the content of water was controlled by Karl Fischer coulometric titration. It is thought that the recycling results will be more rational if the reclaimed electrolyte have same composition with the comparative sample. Therefore, the
compositions of extract were quantified by GC-MS, ICP-OES and NMR. Afterwards, the compositions of extract were replenished with battery grade carbonate solvents and lithium salts based on the formula of the commercial electrolyte (TC-E216#), and then their performance is evaluated under the same conditions.

2.4 Electrochemical Evaluations

Lithium cobalt oxide composite electrode sheets were kindly provided by Coslight Power Co., Ltd. (Harbin, China), which are comprised primarily of 90 wt% lithium cobalt oxide. The thin sheets were punched in a circular shape to be used in coin cells. CR2025-type coin cells were assembled using a Celgard-2400 polypropylene membrane as separator between the Li metal anode and lithium cobalt oxide composite cathode. Galvanostatic charge/discharge was performed at different C-rates using a Neware multichannel battery-testing system (Neware Technology Co., Ltd., Shenzhen, China). Linear sweep voltammetry (LSV) technique was conducted to determine the electrochemical stability window of the electrolytes.\textsuperscript{33} The experimental was performed using a three-electrode, single-compartment configuration where an aluminum electrode as a working electrode (WE) and a Li metal electrode as both the reference and counter electrodes, whereas 1 mL of the electrolyte solution was enclosed in between. The measurements were performed at a scan rate of 1 mV·s\textsuperscript{-1} in the voltage range from 3.0 to 6.0 V. The ionic conductivity of the electrolytes was determined by electrochemical impedance spectroscopy (EIS) that carried out at a frequency range of 1×10\textsuperscript{6} to 0.1 Hz with an oscillating voltage of 5 mV. The electrolyte solution was placed in a Teflon cylindrical cell fitted with two polished stainless steel disks. All the test cells were assembled and sealed in a glove box under an argon atmosphere. All electrochemical measurements were conducted with the CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai, China) at room temperature.
2.5 Characterization

NMR analyses were conducted on a Bruker AVANCE III 400 MHz digital NMR spectrometer. The electrolytes to be studied were placed in 5 mm o.d. tubes and acetone-d$_6$ in a concentric capillary was used for the field/frequency deuterium lock. $^{19}$F and $^{31}$P NMR resonances were referenced to LiPF$_6$ nearby -72.8 ppm and -144.4 ppm, respectively. GC-MS analyses were conducted on an Agilent Technologies 6890A GC with a 5975C mass selective detector and a HP-5ms capillary column. Helium was used as the carrier gas with a flow rate of 1.0 mL·min$^{-1}$.

3. Results and Discussion

3.1 Content of hydrofluoric acid and water

Compared with commercial electrolytes on the market, extracted electrolytes have a few kinds of decomposition products, such as hydrofluoric acid, water and organic phosphates (OPs), and the proportion of constituent system is disturbed or disordered.$^{34-36}$ The hexafluorophosphate anion (PF$_6^-$) in electrolyte may hydrolyze to produce hydrofluoric acid with trace humidity in the carbon dioxide during the extraction process.$^{37, 38}$ Hydrofluoric acid can corrode oxides of battery components to provide more water, followed by further hydrolysis, deteriorating the cycling performance of the battery system.$^{39, 40}$ Therefore, the hydrofluoric acid and water content should be controlled strictly below 50 ppm and 20 ppm, respectively, according to China Chemical Industry Standard (HG/T 4067-2015, Electrolyte lithium hexafluorophosphate). The concentration of the hydrofluoric acid was determined by potentiometric titration with 0.01M KOH in ethanol solution. The potentiometric titration curves of hydrofluoric acid content in electrolyte were shown in Fig.1a, which have characteristic sigmoidal shapes. The inflection points of titration curves represent the equivalence points, which were calculated from the zero
of the second derivative of titration curves in Fig. 1b, 1c and 1d. The $C_{HF}$ (ppm) was calculated by the following equation (1):

$$C_{HF} = \frac{C_{KOH} \cdot V_{KOH} \cdot M_{HF}}{m_{electrolyte}} \times 10^3 \quad (1)$$

Where $C_{KOH}$ is the concentration of potassium hydroxide (mol·L$^{-1}$), $V_{KOH}$ is the volume of titrant used at the corresponding stoichiometric point (ml). $M_{HF}$ is the molar mass of hydrofluoric acid (g·mol$^{-1}$) and $m_{electrolyte}$ is the mass of electrolyte used for potentiometric titration (g).

As much as 149 ppm hydrofluoric acid was measured from the electrolyte of spent LIB. This value increased to 358 ppm after the extraction due to the continuous hydrolysis of PF$_6^-$.

This hydrolysis process simultaneously consumes a certain amount of water in electrolyte, so the water content has decreased from 468 ppm to 310ppm (Table 1). Afterwards, the electrolyte extracts were purified by consecutively passing through anion exchange resin and molecular sieve. The hydrofluoric acid concentrations were dropped from 358 ppm to 37 ppm and the moisture contents were decreased from 310 ppm to 18 ppm, which both satisfied the industry standard.

### 3.2 Component analysis

The organic components of electrolyte extract were analyzed by GC-MS and GC-FID. The total ion current chromatogram (inset in Fig. 2) of the GC-MS analysis revealed the presence of four main organic components in the electrolyte extracts. Mass spectra (Fig. S2) from components of interest are extracted by selecting the correspond peak on the chromatogram. The mass spectrum of the component is matched automatically with official mass spectral database—NIST11, to identify the component. These components are organic solvents EMC (retention time, RT = 6.08
min), DEC (RT = 8.52 min), EC (RT = 14.75 min) and functional additive VC (RT = 7.78 min).

A recent study on the aging products of LIB electrolyte reveals that there are several OPs should be identified except the carbonates, and accurate quantified with LC-MS/MS method developed in literature if necessary. The concentrations of organic components for disassembled electrolytes, extracts, purified electrolytes and reclaimed electrolytes are demonstrated in Fig. 2. The concentrations of VC and EC were reduced after supercritical CO$_2$ extraction. The extraction yields of linear carbonates, EMC and DEC, were higher than cyclic carbonates, VC and EC, which were affected by polarity of carbonates and already intensively discussed in literature.

The contents of LiPF$_6$ were confirmed by PF$_6^-$ analysis using $^{31}$P and $^{19}$F quantitative NMR spectroscopy (qNMR) and Li$^+$ using ICP-OES. The resulting profiles are typical $^{31}$P (Fig. 3a) and $^{19}$F (Fig. 3b) NMR spectra of PF$_6^-$ and its hydrolysis products. The $^{31}$P spectra of PF$_6^-$ consist of an obvious septet at $\delta_P = -144.40$ ppm, as shown in Fig. 3a. The triplet at $\delta_P = -19.36$ ppm represents the primary hydrolysis products (PO$_2$F$_2^-$) of PF$_6^-$. In the spectra of $^{19}$F (Fig. 3b), one of doublet at $\delta_F = -72.56$ ppm is the sign of PF$_6^-$. The other of doublet at $\delta_F = -84.52$ ppm assigned to PO$_2$F$_2^-$. In view of the different experimental conditions and the ability of HF to react with glass NMR tubes, the $^{19}$F qNMR are unsuitable methods to calculate the contents of HF in this paper. The other hydrolysis products cannot be observed in the spectra mainly because the hydrolysis which occurs during the battery cycle life stops at HPO$_2$F$_2$. The existence of triplet in $^{31}$P spectra and the doublet in $^{19}$F spectra suggests that PO$_2$F$_2^-$ anion are not adsorbed onto 4Å molecular sieve. All quantitative results are presented in Table 2. It is thought that the recycling results will be more rational if the reclaimed electrolyte have same composition with the comparative sample. Therefore, the component was replenished as formula of commercial
electrolyte TC-E216#. The contents of electrolyte components are in a usable state theoretically. For further confirming the availability of reclaimed electrolyte, the physical and electrochemical performance would be discussed in the following sections.

3.3 Conductivity Measurement

Ionic conductivity ($\sigma$) of the reclaimed electrolyte plays a pivotal role in the overall performance of LIBs. In view of this, ionic conductivities of the electrolytes were determined as a function of temperature in the range of 10 °C to 50 °C (Fig. 4c). The ionic conductivities were calculated from the a.c. impedance plots and shown in the Fig. 4a and 4b. The bulk resistance ($R_b$) is determined from high frequency intercept on the real axis in complex impedance, then $\sigma$ is calculated by the equations (2).

$$\sigma = \frac{l}{AR_b} \quad (2)$$

where $A$ is the area of the electrodes and $l$ is the distance between electrodes. The ionic conductivity of the reclaimed electrolyte is 0.19 mS cm$^{-1}$ at 293.15 K which is very similar to the commercial electrolyte (0.25 mS·cm$^{-1}$), and increases with the rising of temperature.$^{43,44}$

The ionic conductivity with the course of temperature can be correlated by the Arrhenius Equation (3),

$$\sigma = A \exp\left(\frac{E_a}{RT}\right) \quad (3)$$

where $A$ is the pre-exponential factor and $E_a$ is apparent activation energy. The calculated $E_a$ value of reclaimed electrolyte is 4.53 kJ·mol$^{-1}$, which is very close to the activation energy (5.01 kJ·mol$^{-1}$) of commercial electrolyte. The similar ionic conductivities and activation energy of both electrolytes in quantity suggested that the adding amount of conductive salt is appropriate
for reclaimed electrolyte.\textsuperscript{45} The values of the ionic conductivity and apparent activation energy are summarized in Table S1.

### 3.4 Electrochemical stability window

The electrochemical stability window refers to the potential range of an electrolyte where the solvent or the conductive salt would not take place any electrochemical redox reaction (assuming that the WE and/or the current collector were chemically stable).\textsuperscript{45} Electrochemical stability window is generally determined by LSV of an inert electrode in the selected electrolyte.\textsuperscript{46} The onset of the current in the anodic high potential region is considered to be caused by an electrode-related decomposition process and this onset potential is deemed as the upper limit of the electrolyte stability region.\textsuperscript{47} This potential is determined from the current extrapolated linear intercept on the potential axis in high voltage region. LSV results for commercial and reclaimed electrolyte are shown in Fig. 5. It can be seen that both electrolytes have stability windows up to 5.4 V (\textit{vs.} Li/Li\textsuperscript{+}), but the reclaimed electrolyte showed a very small anodic currents starting at about 3.5V and kept growing gradually till drastic increasing at 5.4 V. This implies that there is slow decomposition of some components in this potential region and electrochemical stability of reclaimed electrolyte is less than commercial electrolyte. However, it is sufficient for the operation of electrode couples such as LiCoO\textsubscript{2}, LiNiO\textsubscript{2}, and LiMn\textsubscript{2}O\textsubscript{4}.

### 3.5 Electrochemical performances

The as-obtained electrolyte system was used in the assembly of coin cells consisting of LiCoO\textsubscript{2} as cathode and Li metal as anode. Fig. 6 shows the typical charge/discharge curves of the assembled lithium ion cells with the reclaimed and commercial electrolyte at the current density of 0.2 C. The characteristics of charge and discharge curves are similar, which indicates that
electrolyte shows good electrochemical performance close to commercial electrolyte. The cells performed at 0.2 C charge/discharge rate with discharge capacity 115 mAh·g⁻¹, which was lower than that with the commercial electrolyte (141 mAh·g⁻¹, Fig. 6). The reversible capacity of the LIB with reclaimed electrolyte remained above 77 mAh·g⁻¹ after 100 cycles at 0.2 C with a capacity retention of 66 % (Fig.7), that is below the cell with commercial electrolyte (remained at 120 mAh·g⁻¹ after 100 cycles at 0.2 C with a capacity retention of 85%). The average Coulombic efficiency (96.2%) for reclaimed electrolyte is similar to the value obtained with commercial electrolyte (99.1%), suggesting the highly reversible Li⁺ insertion/extraction kinetics.⁴⁸, ⁴⁹ It is observed from Fig. 7 that the capacities of both commercial and reclaimed electrolyte faded with the increase of the cycle number. But there is an obvious charge and discharge capacity fading that starting from about 50th cycle in the plots of reclaimed electrolyte. In addition to the intrinsic defects of the LiCoO₂ cathode as reported by other researchers,⁵⁰, ⁵¹ solvent decomposition might be an important reason for the capacity fading. The presence of HPO₂F₂ can further hydrolysis and generate hydrofluoric acid, phosphoric acid and fluorinated phosphates. Particularly, hydrofluoric acid can lead to the decomposition of the active material of the cathode.⁵² Consequently, the cyclic life and capacity retention of the battery is limited.³⁹

4. Conclusions

In conclusion, we have developed a LIB electrolyte recycling method that involves supercritical CO₂ extraction, weakly basic anion exchange resin deacidification, molecular sieve dehydration and components supplement. The conductivity of the resultant electrolyte has been determined as a function of temperature. Electrolytes showed ionic conductivity of 0.19 mS·cm⁻¹ at 20 °C, which is comparable to commercial electrolyte with same composition, and they were also electrochemically stable up to 5.4 V (vs. Li/Li⁺). The Li/LiCoO₂ battery with reclaimed
electrolyte exhibits an initial discharge capacity of 115 mAh·g⁻¹ and the discharge capacity retention of 66 % after 100 cycles at 0.2 C. The reused electrolyte demonstrated acceptable electrochemical performances compared with the commercial electrolyte. Although the reuse of electrolyte relies on the “high-fidelity” of supercritical CO₂ extraction to the products, challenges still exist before considering its practical implementation due to its fast capacity fading in the early cycles. More effective purification approaches for reclaimed electrolyte, such as acid binding substances or fluorinated phosphates removing methods should be available in reclaimed electrolyte. And also more studies on its fading mechanism are needed.

ASSOCIATED CONTENT

Supporting Information

The color contrast of the electrolytes (Figure S1), mass spectra of extracted electrolyte components (Figure S2) and the values of the ionic conductivity and apparent activation energy (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Corresponding author: Changsong Dai

Tel: +86-451-86413751, Fax: +86-451- 86418616, E-mail: changsd@hit.edu.cn

Acknowledgements

We kindly acknowledge the National Natural Science Foundation and for funding of this project (no. 51274075) and the National Environmental Technology Special Project (no. 201009028).
We also thank the Dr. Bo Wang and Dr. Tiantian Gao, at School of Chemistry and Chemical Engineering, Harbin Institute of Technology and for his constant help and suggestions.

References


Figure captions

Scheme 1. Schematic of reclaimed electrolytes from spent lithium-ion batteries.

Figure 1. (a) Potentiometric titration curves and second derivative of titration curves for hydrofluoric acid of electrolyte after (b) disassembly (c) extraction and (d) purification against potassium hydroxide [KOH] = 0.01 M.

Figure 2. Comparison of the chromatograms (GC-FID) for electrolyte in four stages of recycle. The inset is chromatogram (GC-MS) of electrolyte extracts.

Figure 3. $^{31}$P (a) and $^{19}$F (b) NMR spectra of electrolytes containing LiPF$_6$, inset: the magnified impurity peak are compared on the same scale. Blue: Reclaimed; Green: Purified; Red: Extracts; Black: Disassembled.

Figure 4. The a.c. impedance spectra of a) reclaimed and b) commercial electrolyte at 10, 20, 30, 40 and 50 °C. c) The Arrhenius plots of the ionic conductivity at different temperatures.

Figure 5. Linear sweep voltammograms for commercial and reclaimed electrolyte with an aluminum electrode as WE in three electrode configuration at scan rate 1 mV·s$^{-1}$.

Figure 6. Charge/discharge curves of a Li/LiCoO$_2$ cell at 0.2 C with commercial and reclaimed electrolytes, where C corresponded to the current rate.

Figure 7. Cycling performance combined with coulombic efficiency at 0.2 C of commercial and reclaimed electrolyte.

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Table 2. Quantitative results of electrolyte components in four stages of recycle.
Tables

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<th>Extracts</th>
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**Table 2.** Quantitative results of electrolyte components in four stages of recycle.

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Figures and Scheme

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- Pump
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