Research Article

Investigating the oxidation state of Fe from LiFePO₄-based lithium ion battery cathodes via capillary electrophoresis

A capillary electrophoresis (CE) method with ultraviolet/visible (UV–Vis) spectroscopy for iron speciation in lithium ion battery (LIB) electrolytes was developed. The complexation of Fe²⁺ with 1,10-phenantroline (o-phen) and of Fe³⁺ with ethylenediamine tetraacetic acid (EDTA) revealed effective stabilization of both iron species during sample preparation and CE measurements. For the investigation of small electrolyte volumes from LIB cells, a sample buffer with optimal sample pH was developed to inhibit precipitation of Fe³⁺ during complexation of Fe²⁺ with o-phen. However, the presence of the conducting salt lithium hexafluorophosphate (LiPF₆) in the electrolyte led to the precipitation of the complex [Fe(o-phen)_3](PF₆)₂. Addition of acetonitrile (ACN) to the sample successfully redissolved this Fe²⁺-complex to retain the quantification of both species. Further optimization of the method successfully prevented the oxidation of dissolved Fe²⁺ with ambient oxygen during sample preparation, by previously stabilizing the sample with HCl or by working under counterflow of argon. Following dissolution experiments with the positive electrode material LiFePO₄ (LFP) in LIB electrolytes under dry room conditions at 20°C and 60°C mainly revealed iron dissolution at elevated temperatures due to the formation of acidic electrolyte decomposition products. Despite the primary oxidation state of iron in LFP of +2, both iron species were detected in the electrolytes that derive from oxidation of dissolved Fe²⁺ by remaining molecular oxygen in the sample vials during the dissolution experiments.

Keywords:
Capillary electrophoresis / Cathode / Electrolytes / Iron speciation / Lithium ion battery / Transition metal dissolution

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1 Introduction

The superior high energy densities (in particular per volume) at low costs pave the way for LIBs to become the most commonly used rechargeable battery systems [1–4]. The positive electrode materials of customary LIBs are mainly based on layered lithium metal oxides (LMO, M = Ni, Co, Mn, Al), on spinel type LiMn₂O₄ (LMO) or on olivine type (LMPO₄) with LiFePO₄ (LFP) as most promising example [5–9]. In comparison to layered materials containing nickel and cobalt, from the point of metal costs, the iron-based LFP is expected to be a cheaper, and also a safer alternative with high structural stability and good rate capability [5,10–13]. However, LFP-based cells also show ongoing capacity loss with increasing cycle number. The capacity loss is mainly associated with side reactions of the electrolyte, resulting in the loss of active lithium and finally to a lower battery lifetime [14–21]. As for other transition metal ions like nickel, cobalt, and manganese, deposited iron on the negative electrode could accelerate these side reactions [22–29].

The dissolution of iron from LFP-based cathodes was first investigated by Iltchev et al. [30]. In comparison to...
manganese dissolution from LMO, dissolution of iron was less pronounced for LFP. However, presence of water impurities in the electrolyte strongly accelerated the iron dissolution [30]. The reported effects of dissolved iron on cell performance and on capacity loss were partially controversial. While Liu et al. indicated no significant impact of dissolved iron on the performance, most studies demonstrated an increased capacity loss due to deposited iron at the anodes surface [14]. Liu et al. detected dissolved iron in electrolytes of LFP|graphite cells, but investigations of the graphite-based negative electrodes with energy-dispersive X-ray spectroscopy showed no deposited iron within the limits of detection. Therefore, no effects of dissolved iron on the cell performance were presumed and other effects were presumed to be primary responsible for capacity loss [14]. In contradiction, Amine et al. demonstrated that Fe$^{2+}$ dissolution, deposition, and possible reduction on the surface of the negative electrode strongly correlated with capacity loss. Hence, ongoing electrolyte decomposition takes place on the deposited metallic iron, leading to increased cell impedance and finally to lower capacity retention. Iron dissolution was mainly associated to an ion exchange reaction between iron in LFP and protons from formed HF in organic solvent-based electrolytes with LiPF$_6$ as conducting salt. In case of lithium bis(oxalato)borate (LiBOB) as conducting salt, higher capacity retentions and much less dissolved iron were received due to the absence of HF [24]. Striebel et al. also confirmed these observations, but detected deposited iron oxide instead of metallic iron on the anodes surface [25]. Further studies showed that acid scavengers in electrolytes significantly reduce Fe$^{2+}$ dissolution [31]. Moreover, another dissolution mechanism proposed by Zaghib et al. correlates iron dissolution and iron oxide impurities in LFP [32]. The influence of Fe$^{2+}$ in the electrolyte on cell performance was investigated by Lai et al., indicating reduction of Fe$^{3+}$ at the surface of the negative electrode and subsequent accelerated electrolyte decomposition and blocking of reversible intercalation of lithium ions into the graphite electrode [27].

In order to enable a better understanding of the dissolution mechanism(s) and possible negative effects of iron dissolution on the cell performance, investigations regarding the oxidation states of the dissolved iron in LIB electrolytes are mandatory. Unlike for manganese, no species analysis was performed for iron in LIB electrolytes so far [33–35]. CE has a high capability for iron speciation in aqueous solutions as demonstrated in previous studies using complexing agents like o-phen and EDTA for stabilization of Fe$^{2+}$ as well as Fe$^{3+}$ and to enhance their solubility [36–38]. Thus, CE is an optimal technique for the investigation of traces of Fe$^{2+}$ or Fe$^{3+}$ in LFP for quality control [38]. The use of an alkaline borate-based running buffer at pH 9.2 enabled a fast separation of the oppositely charged Fe$^{2+}$/o-phen and Fe$^{3+}$/EDTA-complex in a single run [36, 37]. Based on these studies, a CE method for iron speciation in organic carbonate-based electrolyte samples was developed and applied on dissolved iron species after dissolution experiments with LFP.

2 Materials and methods

2.1 Capillary electrophoresis

An Agilent Technologies 7100 CE System (Santa Clara, CA, USA) with UV–Vis detection (Long-life Deuterium Lamp (8-pin) RFID tag, Santa Clara, CA, USA) was used for the investigation of Fe$^{2+}$ and Fe$^{3+}$. Fused silica capillaries with 75 μm inner diameter, 365 μm outer diameter, and 50 cm length (41.5 cm effective length) were obtained from Polymicro Technologies (Phoenix, AZ, USA). Capillaries were preconditioned by rinsing the capillaries for 500 s with 0.1 mol/L NaOH (1 mol/L Titrisol® Merck, Darmstadt, Germany) and 500 s with Milli-Q water (18.2 mΩ cm, Milli-Q Advantage A10, Merck). Subsequently, capillaries were flushed 2000 s with running buffer for equilibration. Before and after each run, capillaries were reconditioned with running buffer for 300 s and 60 s, respectively. The separation conditions were +30 kV with a voltage ramp of 30 s at a constant temperature of 25°C. Samples were injected hydrodynamically with a pressure of 50 mbar for 7 s, followed by an injection of running buffer under same conditions. Detection was performed according to literature at 245 nm for Fe$^{2+}$, 266 nm for Fe$^{3+}$, and 254 nm for simultaneous analysis of both species [36, 37].

2.2 Preparation of running buffer, sample buffer, and standards

A running buffer (25 mM, pH 9.2) with sodium tetraborate (Na$_2$B$_4$O$_7$, for analysis, Merck) was diluted with Milli-Q water. 1,10-phenantroline chloride monohydrate (o-phen, ≥99.5%, Merck) was added to the running buffer resulting in a concentration of 0.2 mM. The sample buffer (20 mM ammonium phosphate) was prepared using phosphoric acid and ammonia solution. Both chemicals were obtained from Merck (H$_3$PO$_4$ (85%); NH$_3$ (25%), Emsure®). 100 mM o-phen was added to the sample buffer and the pH was adjusted to 2.1 (Profiltrone 6.0255.110, Metrohm, Herisau, Switzerland; Software: Tiamo 2.4).

An ICP-standard (1000 mg/L, TraceCert®, Sigma–Aldrich, Buchs, Switzerland) was used for Fe$^{3+}$. The Fe$^{3+}$-standard (1000 mg/L) was prepared by dissolving iron(II) chloride tetrahydrate (for analysis, Emsure®, Merck) in 0.2% HCl (37%, Suprapur™, Fisher Scientific, Loughborough, UK). The total amount of iron was determined via inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Analytical Instruments GmbH, Kleve, Germany) with an axial positioned plasma torch according to Vortmann and Evertz et al. [19, 39] The prepared Fe$^{3+}$-standard solution was stored at 5°C.

2.3 Determination of the recovery rate

The recovery rate was determined with electrolyte solutions containing Fe$^{2+}$ and Fe$^{3+}$. For this, iron(II) chloride and
iron(III) chloride hexahydrate (97%, Sigma–Aldrich, Steinheim, Germany) were dissolved in electrolyte (1 M LiPF6 in ethylene carbonate (EC)/ethyl methyl carbonate (EMC), 50:50 wt%, Selectlyte™ LP50, BASF, Independence, OH, USA). In case of Fe²⁺, a saturated solution was prepared for a suitable Fe²⁺-concentration. The remaining salt was removed by centrifugation at 8500 rpm for 10 min (Galaxy 5D, VWR, Radnor, PA, USA). The total iron concentrations of the obtained solutions were determined by ICP-OES. The quantification of Fe²⁺ and Fe³⁺ in electrolytes was conducted via CE–UV–Vis with external calibration.

### 2.4 Storage experiments of LFP in lithium ion battery electrolyte

Samples containing LFP (100 mg, P13F, TATUNG Fine Chemicals Co., Taipei, Taiwan) and 1 mL electrolyte (1 M LiPF₆ in EC/EMC, 50:50 wt%, Selectilyte™ LP50, BASF) were prepared in a dry room (dew point: −65°C, H₂O: 5.4 ppm). The water content in the electrolyte (<30 ppm) was determined according Henschel et al. via Karl–Fischer titration (Büchi®, B-585, Essen, Germany) at 120°C under vacuum for 22 days. Afterward, the LFP-particles were removed by centrifugation (8500 rpm, 10 min, Galaxy 5D, VWR). The sample preparation was performed according to Pozdniakova et al. by first stabilizing Fe²⁺ with o-phen and finally by complexation of Fe³⁺ with EDTA [37]. This sample preparation order inhibits the oxidation of Fe²⁺ in presence of EDTA in contact with air and the formation of the more stable Fe³⁺-EDTA-complex [37]. Furthermore, an optimal sample pH is necessary to prevent the precipitation of Fe³⁺ (<pH 2.4) and to enable optimal formation of the Fe²⁺-o-phen-complex (>pH 2) [37]. For small samples volumes usually obtained from LIBs, a pH-adjustment without buffer would lead to high dilution of the sample. Therefore, a sample buffer (20 mM ammonium phosphate, pH 2.1) was applied for optimal complexation and stabilization conditions. However, matrix effects occurred at sample buffer concentration exceeding 200 mM that resulted in broader and less intense Fe²⁺ and Fe³⁺-signals and a decreased peak area for Fe³⁺ of 37.6% (Fig. 1A and B). No changes in integrated peak areas were observed for 20 and 50 mM sample buffers. Therefore, the lowest buffer concentration (20 mM) was used. Moreover, the Fe³⁺-signal shifted to higher migration times using higher sample buffer concentrations (Fig. 1B). However, compared to further electropherograms in this work, an overall increased migration time of Fe³⁺ was observed for these measurements. The shift in migration times was caused by the adsorption of the red colored Fe²⁺-o-phen complex on the capillary wall at the capillary inlet after multiple injections, which affected the charge of the capillary wall and led to a less strong electroosmotic flow. The removal of the adsorbed Fe²⁺-complex with organic solvents or the use of new capillaries resulted in reduced migration times of the Fe³⁺-complex. In the following step, the optimal o-phen concentration in sample buffer to stabilize the Fe³⁺ was determined to be 100 mM. After dilution, an o-phen concentration of 12.5 mM was obtained in the prepared sample. At lower o-phen concentrations, the peak area of Fe³⁺ decreased while an additional Fe²⁺-signal appeared due to the oxidation of Fe²⁺ (not shown). However, no reduction of the Fe³⁺ was observed during the sample preparation according to literature [37].

In contrast to previously reported CE methods for iron speciation, the running buffer in this work only contained o-phen as auxiliary ligand without EDTA [36,37]. In a running buffer with o-phen and EDTA, partly decomposition of

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the Fe$^{2+}$-complex during CE measurements was observed. This decomposition resulted in an increased baseline between the Fe$^{2+}$ and the o-phen signal (Fig. 2A). A comparable decomposition of the Fe$^{2+}$-complex during electrophoresis was observed without o-phen in the running buffer. Furthermore, small needle-like crystals of o-phen were detected in the running buffer that is why dissolved o-phen was no longer present to stabilize the Fe$^{2+}$-complex during CE measurements. A running buffer without EDTA showed no precipitated o-phen and no decomposition of the Fe$^{2+}$- and Fe$^{3+}$-complexes during electrophoresis (Fig. 2B). Consequently, a pre-capillary complexation for Fe$^{3+}$ with EDTA was sufficient. The developed method enabled the separation of Fe$^{2+}$ and Fe$^{3+}$ in <4 min.

The proof of principle experiment in a LIB electrolyte matrix was conducted with samples prepared with Fe$^{2+}$, Fe$^{3+}$ (0.179 mM each), and 1 vol% of electrolyte containing LiPF$_6$ (1 M) as conducting salt. After dilution with the sample buffer, a red colored and slightly soluble precipitation of [Fe(o-phen)$_3$]PF$_6$ was observed. However, no precipitation occurred with anions like F$^-$ from the conducting salt LiPF$_6$ or Cl$^-$, NO$_3^-$, or SO$_4^{2-}$ from iron standards. After centrifugation, the supernatant solution was investigated with CE-UV-Vis. The electropherogram showed only a small remaining Fe$^{2+}$-signal (Fig. 3A) demonstrating the precipitation of [Fe(o-phen)$_3$]PF$_6$. However, the Fe$^{3+}$-EDTA-complex was not affected by the electrolyte. The precipitated [Fe(o-phen)$_3$]PF$_6$ was highly soluble in protic organic solvents such as methanol, ethanol, and ACN. Therefore, these organic solvents were added to the samples in various concentrations to prevent the precipitation of the Fe$^{2+}$-complex. ACN fully prevented the precipitation of the Fe$^{2+}$-complex.
Figure 3. Electropherograms for Fe$^{2+}$ and Fe$^{3+}$ (0.179 mM each) with 1 vol% LIB electrolyte (A) and with 1 vol% LIB electrolyte and 37.5 vol% ACN (B).

Table 1. Method validation considering relative standard deviations of peak areas and migration times ($n = 6$) as well as linear range, LODs, and LOQs for Fe$^{2+}$ and Fe$^{3+}$.

|                | Fe$^{2+}$ | Fe$^{3+}$ |
|----------------|-----------|-----------|
| Peak area variation [%] | 0.9       | 1.6       |
| Migration time variation [%] | 0.1       | 1.0       |
| Linear range [μg/L] | 5.0–50 × 10$^3$ | 25.0–50 × 10$^3$ |
| $R^2$            | 0.9999    | 0.9998    |
| LOD [μg/L]      | 18.4      | 187.7     |
| LOQ [μg/L]      | 68.2      | 693.9     |

at a concentration of 37.5 vol%. The electropherogram of this sample showed a fully recovered Fe$^{2+}$-signal (Fig. 3B). A negative effect of ACN on the Fe$^{3+}$-signal was not observed. Since the precipitation directly occurred during dilution with sample buffer, inevitable loss of Fe$^{3+}$ can be the consequence. To overcome this issue, ACN was mixed with the sample buffer and also with the EDTA solution in a ratio of 1:1 (v/v) before dilution with electrolytes. Furthermore, ACN in the sample reduced the adsorption of the Fe$^{2+}$-complex at the capillary inlet and led therefore to a higher reproducibility.

In the next step, the reproducibility and the stability of migration times for both iron species were determined after multiple injections (Table 1; 0.179 mM each, $n = 6$). Furthermore, the LOD and LOQ were determined according to DIN 32 645 using a multi-level-calibration ($N = 10$, $n = 3$).

Long-term effects as clogging of the capillary, peak shifting, or changing signal intensities were not observed due to ACN in the sample. Moreover, both complexed iron species were stable and loss of species due to oxidation or reduction were not detected during daily measurements.

For recovery rates, solutions of FeCl$_2$ and FeCl$_3$ carbonate-based LIB electrolyte were prepared. In case of Fe$^{2+}$, a saturated solution was prepared to obtain suitable concentrations of Fe$^{2+}$ in the electrolyte. In contrast, FeCl$_3$ dissolved faster and more easily into the LIB electrolyte, leading to higher concentrations of dissolved Fe$^{3+}$. Furthermore, dissolved Fe$^{2+}$ was unstable in the electrolyte and fast oxidation was observed in contact with atmosphere (intense yellow electrolyte solution). This electrolyte showed only a low Fe$^{3+}$-fraction of 41.2%. Due to the air sensitivity of Fe$^{2+}$ in LIB electrolytes, FeCl$_2$ was predried under vacuum and the sample was prepared in an argon glovebox. Under atmosphere, the recovered electrolyte was directly stabilized with 0.5% HCl in a ratio of 1:1 (v/v) to prevent oxidation. The determined Fe$^{2+}$ recovery increased to 80.2%. Alternatively, the sample preparation was performed under argon counterflow to improve antioxidative conditions. With an Fe$^{2+}$-fraction of 79.3%, both sample preparation methods showed similar results. Analysis of the predried FeCl$_2$ showed an Fe$^{3+}$-fraction of 4.6% due to oxidation of Fe$^{2+}$ during the drying process. Since Fe$^{3+}$ showed a higher solubility compared to Fe$^{2+}$, an increased amount of Fe$^{3+}$ in the electrolyte was assumed. Because oxidation of Fe$^{2+}$ during the drying process cannot be fully prevented, the sum of the Fe$^{2+}$ and Fe$^{3+}$-concentration was used for the calculation of the recovery rate for Fe$^{2+}$. Based on this premise, the determined recovery rate for Fe$^{2+}$ was 99.4% and for Fe$^{3+}$ 98.1%.

3.2 Dissolution of iron species in LIB electrolytes

Several studies on iron dissolution from LFP into LIB electrolytes claimed an ion exchange reaction between protons from formed acidic decomposition products of the electrolyte and Fe$^{2+}$ in the LFP [24, 25, 31]. Commercially applied LIB electrolytes are comprised of the conducting salt LiPF$_6$ and a mixture of different cyclic and linear organic carbonates [1, 41–43]. During charge–discharge cycling and especially at
Elevated temperatures, the conducting salt can decompose and form different acidic products like HF or difluorophosphoric acid [44–50]. Thus, Koltypin et al. postulated a higher iron dissolution at elevated temperatures due to an increased HF formation [31].

Iron dissolution experiments were performed in headspace vials with LFP in LiPF₆-based electrolytes at 20 and 60°C for 22 days under dry room conditions, standardly used for LIB cell assembly [51]. No iron species were detected in electrolytes after storage at 20°C (black line) within the LODs, even at increased electrolyte concentrations (Fig. 4A; reduced dilution factor of 1:10, v/v). After storage at 60°C, both iron species were detected in electrolytes (Fig. 4A, red line) with Fe³⁺ as the main iron species (Fig. 4B; 91.2–92.6%).

Considering the oxidation state of iron in lithiated (discharged) LFP, dissolution of Fe²⁺ in the first step can be attributed to the formation of acidic decomposition products in the electrolyte and a following ion exchange reaction between H⁺ and Fe²⁺ (Fig. 5) [24,31]. However, minor dissolution of Fe⁺ cannot be excluded due to some Fe³⁺-impurities in LFP [38]. Afterward, dissolved Fe²⁺ was readily oxidized to Fe³⁺ in presence of remaining molecular oxygen in the headspace vial. The formation of insoluble iron(III) oxides from the reaction of Fe²⁺ with oxygen was not favored. Otherwise, no Fe³⁺ would have been detected. The reduced oxygen species, like superoxide (O₂⁻), probably underwent further reactions with organic carbonates in the electrolyte. Previous investigations on reduced oxygen species in organic carbonate-based electrolytes demonstrated that superoxide reacts via a nucleophilic attack with cyclic carbonates in a ring-opening reaction (Fig. 5) [52]. These nucleophilic carbonate species can then undergo further reactions with other (linear) carbonate solvents in the electrolyte.

The dissolution experiments in this work should be considered as preliminary studies for future dissolution experiments in electrolytes from real LIB cells. In case of LIB cells, built under inert gas, the acidic dissolution of Fe²⁺ from the cathode material LFP as suggested in previous studies is plausible [24,31]. However, no species analysis was performed so far to investigate also the acidic dissolution of Fe³⁺ from discharged LFP, when iron is in the oxidation state +3. Moreover, some commercial LIB cells and for sure laboratory-built battery cells may have remaining air-filled cavities after assembly under dry and/or protective gas conditions. Therefore, not only the reported iron deposition at the graphite
anode but also the reaction of dissolved Fe\^{3+} with molecular oxygen could lead to accelerated electrolyte decomposition and ongoing capacity loss of these cells. Hence, these topics should be subject for future work.

4 Concluding remarks

In summary, a new CE method for iron speciation in LIB electrolytes was successfully developed for prospective detailed quantitative investigations on iron dissolution in LIBs and resulting negative effects of the dissolved iron species on cell performance. Optimal stabilization and complexation conditions for dissolved iron species were achieved with a sample buffer. To overcome the precipitation and loss of the Fe\^{3+}-complex by LiPF\(_6\) in LIB electrolytes as [Fe(o-phen)].[PF\(_6\)]., ACN was added to the sample in advance. Thus, the separation of both iron species in LIB electrolytes was achieved in <4 min with detection limits in a low μg/L range.

Dissolution experiments with LFP at 20 and 60°C in LIB electrolyte only revealed iron dissolution at elevated temperatures due to the formation of acidic electrolyte decomposition products. Both iron species were detected, however with Fe\^{3+} as the main species due to the oxidation of dissolved Fe\^{2+} by molecular oxygen under dry room conditions. Since Fe\^{3+} did not precipitate as iron(III) oxide, further reactions of the reduced oxygen species with organic carbonates via a nucleophilic attack can be postulated.

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5 References

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