Research Article

**Mn**$^{2+}$ or Mn$^{3+}$? Investigating transition metal dissolution of manganese species in lithium ion battery electrolytes by capillary electrophoresis

A new CE method with ultraviolet–visible detection was developed in this study to investigate manganese dissolution in lithium ion battery electrolytes. The aqueous running buffer based on diphosphate showed excellent stabilization of labile Mn$^{3+}$, even under electrophoretic conditions. The method was optimized regarding the concentration of diphosphate and modifier to obtain suitable signals for quantification. Additionally, the finally obtained method was applied on carbonate-based electrolytes samples. Dissolution experiments of the cathode material LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (lithium nickel manganese oxide [LNMO]) in aqueous diphosphate buffer at defined pH were performed to investigate the effect of a transition metal-ion-scavenger on the oxidation state of dissolved manganese. Quantification of both Mn species revealed the formation of mainly Mn$^{3+}$, which can be attributed to a disproportionation reaction of dissolved and complexed Mn$^{2+}$ with Mn$^{4+}$ at the surface of the LNMO structure. It was also shown that the formation of Mn$^{3+}$ increased with lower pH. In contrast, dissolution experiments of LNMO in carbonate-based electrolytes containing LIPF$_6$ showed only dissolution of Mn$^{2+}$.

**Keywords:**
Capillary electrophoresis / Electrolytes / Lithium ion battery / Manganese speciation / Transition metal dissolution

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Additional supporting information may be found online in the Supporting Information section at the end of the article.

1 Introduction

Lithium ion batteries (LIBs) are the benchmark rechargeable battery systems due to comparably higher energy densities at low costs [1–6]. The cathode materials are commonly composed of layered lithium metal oxides (LMO$_2$, M = Ni, Co, Mn, Al) or spinel-type LiMn$_2$O$_4$ (LMO) and lithium nickel manganese oxide (LNMO) [7–10]. In the first charge–discharge cycles, a solid electrolyte interphase (SEI) is formed at the anode surface, protecting the electrolyte from further decomposition [11–14]. During LIB operation, transition metal (TM) ions can dissolve from the cathode, migrate through the electrolyte to the anode, and are subsequently incorporated into the SEI or are reduced to metal [15–19]. These effects eventually lead to increased cell impedance, more side reactions, and finally to reduced life [16, 20, 21]. Therefore, it is important to prevent the dissolution of TMs in LIBs, their migration to the anode, or to enhance the tolerance of LIBs regarding the dissolved TMs [22–27].

Dissolution of manganese was observed for a variety of cathode materials [16, 17, 20, 21, 28–33]. In addition to dissolution mechanisms like corrosion or structural deformation, dissolution by disproportionation reaction of surficial Mn$^{3+}$ to Mn$^{4+}$ and soluble Mn$^{2+}$ is mainly reported in the literature [7, 17, 18, 20, 21, 29, 30, 34–36]. Several more recent studies found dissolved manganese to be mainly in oxidation state +3 not in +2, which is in contradiction to established reports. Therefore, the capability to determine the oxidation states of manganese ions is a key to reveal the actual dissolution mechanism(s).

Usually, spectroscopic methods like X-ray absorption near-edge structure spectroscopy (XANES) were applied to investigate the manganese species, however without the
the possibility of quantification. Terada et al. showed by XANES measurements of electrolytes from LMO||Li-metal cells only the presence of Mn$^{3+}$ [31]. Furthermore, it was shown that the deposited manganese on anodes was predominantly in oxidation state $+2$ [16]. Jerry et al. used various spectroscopic techniques to study dissolution from LNMO. With these techniques, Mn$^{2+}$ complexes were detected, which were claimed to be formed by oxidation of electrolyte at the cathode surface. After dissolution, Mn$^{3+}$ was reduced to Mn$^{2+}$ before incorporated into the SEI [37]. Li et al. investigated separators from LMO-based cells after cycling at 50°C, containing polymeric azA-15-crown-5 ethers as Mn ion scavenging agent with XANES, revealing an average oxidation state close to $+3$ [25]. Other studies showed the dissolution of both manganese species for LNMO and LMO cathode materials in standard carbonate-based electrolytes after storage and battery operation, with a high fraction of Mn$^{3+}$ [38, 39].

To enable a simultaneous separation and quantification of Mn$^{2+/3+}$ in carbonate-based electrolytes of LIBs, a complementary new CE method is introduced in this work. The CE allows the separation and detection of several metal ions and also of different soluble oxidation states of TMs in a single run [40–44]. However, the investigation of Mn$^{2+/3+}$ was not performed with a CE before. It is obvious that the CE is getting more common in LIB research, for example, for the investigation of electrolyte decomposition products or for the quantification of TMs in cathode materials [45–50]. The investigation of the oxidation states of dissolved TMs is a new topic in LIB research and the CE might play a major role for this. Even more, this developed method can also be interesting for other research fields [51, 52]. Finally, the dissolution of Mn$^{2+}$ from LNMO cathode material was investigated after different storage tests at defined conditions.

## 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 quantification of Mn$^{2+}$ and Mn$^{3+}$. Fused silica capillaries with 75 μm inner diameter, 365 μm outer diameter, and 100 cm length were obtained from Polymicro Technologies™ (Phoenix, AZ, USA).

For preconditioning, the capillaries were flushed with 1 vol% HCl (30%, Suprapure®; Merck, Darmstadt, Germany) for 500 s, 500 s with Milli-Q water (18.2 mΩ cm, Milli-Q Advantage A10; Merck), 750 s with running buffer, 150 s with 1 vol% HCl and 150 s with Milli-Q water. This procedure was repeated at each measurement day. HCl was purified before use by subboiling distillation (Savillex® DST-1000, Eden Prairie, MN, USA). Before each run, the capillary was flushed with 1 vol% HCl for 150 s, 150 s with Milli-Q water, and 300 s with running buffer. After each measurement, the capillary was flushed again with 1 vol% HCl for 150 s and 150 s with Milli-Q water. The temperature was set constant to 24°C. The separation was performed at ~30 kV. Samples were injected hydrodynamically with a pressure of 50 mbar for 5 s. Additionally, running buffer was injected afterward at the same conditions.

### 2.2 Preparation of running buffer, sample buffer, and standards

Tetrabutylammonium pyrophosphate decahydrate was purchased from Arcos-Organics (99.4%, Geel, Belgium) and CTAB (99%) from Sigma-Aldrich (St. Louis, MO, USA). Milli-Q water (18.2 mΩ cm; Milli-Q Advantage A10, Merck) was used for dilution. The pH value was adjusted with HCl using a pH-electrode from Metrohm AG (Profitore 6.0255.110; Herisau, Switzerland; Software: Tiamo 2.4). The sample buffer was prepared in the same way, without adding CTAB, to enable accurate sample handling.

Note that 1000 mg/L ICP-standards from TraceCert® (Sigma Aldrich, Buchs, Switzerland) were used for Mn$^{2+}$ and Cu$^{2+}$ (as internal standard). These standards were diluted with sample buffer.

A total of 1000 mg/L Mn$^{3+}$-standard solution was prepared by diluting manganese(III) acetate dihydrate (97%, Sigma-Aldrich) in diphosphate-buffer (182 mM, pH 7, adjusted with HCl). Due to water sensitiveness of Mn$^{3+}$, the weighing was done in a dry room (Dew point: $-65^\circ$C, H$_2$O: 5.4 parts per million). A red-violet colored solution was obtained and no precipitations of MnO$_2$ from disproportionation reaction were observed. The prepared Mn$^{3+}$ standard solution was stored at 5°C. For quantitative applications, the total amount of manganese of the standard was determined by inductively coupled plasma optical emission spectrometry (Spectro ARCOS, Spectro Analytical Instruments, Kleve, Germany, see [28]).

### 2.3 Determination of the recovery rate

For the determination of the recovery rate, a concentrated Mn$^{3+}$-solution was prepared by dissolving Mn(III) acetate in electrolyte (1 M LiPF$_6$ in ethylene carbonate/ethyl methyl carbonate = 1:1wt%, Selectilyte® LP50; BASF, Independence, OH, USA). The water content in the electrolyte was less than 30 ppm. The total concentration of manganese was determined by ICP-optical emission spectrometry. Meanwhile, the amount of Mn$^{2+}$ and Mn$^{3+}$ in the electrolyte was performed with the developed CE-method and an external calibration using the prepared standards.

### 2.4 The effect of a TM-ion-scaevenger on the oxidation state of dissolved manganese

Note that 5 mg of synthesized nonstoichiometric LNMO powder was immersed in 15 mL centrifuge tubes (Ultra High Performance; VWR, Radnor, PA, USA) with 5 mL of 27 mM
diphosphate buffer at pH of 3, 5, and 7. The pH was adjusted with HCl. The samples were shaken at 20°C with 250 rpm (Advanced Digital Shaker 3500; VWR) for 10 weeks. The synthesis route of LNMO was published before and is described in detail in the Supporting Information [28].

2.5 Storage experiments of LNMO/electrolyte samples

Samples with LNMO powder (50 mg) immersed in 1 mL electrolyte (1 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate = 1:1 vol%, Selectlyte LP50; BASF) were prepared in an argon glovebox. The samples were stored in self-made headspace vials (10 mL) made out of polyetheretherketone. Vials and crimp tops (Cap BI 20 mm Si/PTFE, hole 8 mm; 45°, A 3 mm, VWR™) were dried before use at 60°C in a vacuum drying chamber (Binder, Tuttlingen, Germany) for 2 days. After sample preparation, the vials were sealed with crimp tops and additionally from outside with silicone rubber (Adhesive Sealant; Momentive Performance Materials GmbH, Leverkusen, Germany). The samples were stored at 20°C and in a climate chamber (Binder) at 60°C for 10 weeks.

2.6 Sample preparation

Electrolyte samples were opened in a dry room to prevent contamination with water. Recovered electrolyte was transferred to 2 mL centrifuge vials (Safe-Lock Tubes; Eppendorf, Hamburg, Germany) and remaining residues were removed by centrifugation at 8,500 rpm for 10 min (Galaxy 5D; VWR). Afterward, the samples were diluted with sample buffer.

3 Results and discussion

3.1 Method development

Unlike in water-free organic solvents, Mn³⁺-ions are not stable in aqueous solutions due to favored disproportionation reaction of Mn³⁺ with H₂O to Mn²⁺ and Mn⁴⁺ [53]:

\[ 2\text{Mn}^{3+} + 2\text{H₂O} \rightarrow \text{Mn}^{2+} + 4\text{H}^{+} + \text{MnO}_2 \]  

(1)

Consequently, dissolved Mn³⁺ has to be stabilized by suitable ligands for CE measurements with aqueous buffers, even under electrophoretic conditions of the CE. Two requirements have to be met by the ligand: (1) formation of a stable Mn³⁺-complex and (2) inertness against oxidation by Mn⁴⁺. Many organic complexing ligands such as EDTA, citrate, or others show storage limitations due to oxidation by Mn⁴⁺ over time, and therefore cannot be used for quantification [53, 54]. In contrast, inorganic diphosphate is redox inactive and forms a stable complex with Mn³⁺. In excess of diphosphate compared to Mn³⁺, it stabilizes the Mn³⁺-ion over a wide pH range of 1–8 [53–56]. Consequently, diphosphate has already been used as complexation agent in CE running buffer for quantification of formed Mn³⁺ in case of the reaction of citric acid with the mineral birnesite (M,Mn³⁺⁺/2O₄), while quantification of Mn⁴⁺ was not performed [57]. In this work, diphosphate was not only used for complexation of Mn³⁺ and Mn⁴⁺, but also as buffering agent for electrophoresis.

Due to expected negatively charged manganese complexes, the separation was performed at negative polarity. CTAB as dynamic modifier was added to reverse the electroosmotic flow. The optimal buffer conditions for separation of Mn²⁺ and Mn⁴⁺ were found to be 27 mM diphosphate and 400 µM CTAB at a pH of 3.1, adjusted with HCl. The detailed CE method optimization steps are shown in the Supporting Information. Cu²⁺ was used as internal standard because it forms a stable diphosphate complex, which absorbs in the UV range, and does not interfere with the manganese species. TMs like nickel or cobalt, which are often used in combination with manganese for LIB cathode materials, were not detectable with this developed CE method. A possible reason for this could be the instability of the Ni²⁺ and Co²⁺ diphosphate complexes at this low pH, why both species stayed positive in the running buffer and did not reach the detector during measurement.

In the electropherogram (enlarged section, Fig. 1), three signals of interest showed up in migration order Mn²⁺ > Cu²⁺ > Mn⁴⁺. The EOF (negative signal) was detected later than the Mn⁴⁺-signal at 12.3 min. The migrating NO₃⁻ at 4.4 min, stemming from the Mn⁴⁺ and Cu²⁺ standards, was omitted for better clarity. The faster migration times of the TM compared to the EOF confirmed the formation of negatively charged TM-diphosphate complexes. Structural investigations of the formed complexes by high-resolution mass spectrometry were performed via direct infusion into LCMS-IT-TOF™ (see Supporting Information), revealing coordination of the metal ions by two diphosphate ligands. Coordination by just one diphosphate can be ruled out as suggested earlier [53].

Figure 1. Zoom into the electropherogram of a sample containing 10 mg/L Mn³⁺, Cu²⁺, and Mn⁴⁺ using 27 mM diphosphate and 400 µM CTAB as running buffer (pH 3.1), capillary length: 95 cm, voltage: −30 kV, UV detection at 220 nm.
Figure 2. (A) Peak heights of each analyte (10 mg/L each) versus wavelength. For better overview of the results, the peak heights were fitted. (B) Baseline noise versus wavelength.

For optimal signal intensities of the three TM complexes, a Mn$^{3+}$, Cu$^{2+}$, and Mn$^{2+}$ containing sample (5 mg/L each) was measured with the developed CE method at defined wavelengths between 200 and 320 nm (10 nm steps). The resulting signal heights for each TM complex were plotted against the related wavelength and the data points for each species were interpolated for a clearer overview (Fig. 2A). The use of the signal heights allows the elimination of additional absorption by the running buffer. Even more, the baseline noise was determined for each measured wavelength, why then the noise can be also considered into decision of the optimal wavelengths (Fig. 2B).

The Mn$^{3+}$-complex (red line) shows two peak maxima at 210 and 260 nm with approximately similar intensities. At ≥260 nm, the peak height decreases steadily. The peak height of the Cu$^{2+}$-complex (blue line) increases from 200 nm up to a maximum at 220 nm and decreases steadily afterwards. Unlike the other complexes, no peak was observed for the Cu$^{2+}$-complex from 260 nm onwards. In contrast to the complexes of Mn$^{3+}$ and Cu$^{2+}$, the Mn$^{2+}$-complex (green line) did not show any maximum. The highest peak was detected at 200 nm. With increasing wavelengths, the peak height decreased steadily, with a small shoulder at 260 nm. The baseline noise was also plotted against the related wavelengths (Fig. 2B). At 200 nm, the noise was highest with 0.025 mAU and drops down to a nearly constant value of 0.007 mAU. By comparing peak heights and noise, wavelengths of 210 and 260 nm were chosen for Mn$^{3+}$ and 220 nm for Cu$^{2+}$. Due to a lower signal to noise ratio at 200 nm, 210 nm was chosen for the detection of Mn$^{2+}$. Due to the comparable high signal intensities of all three TM complexes at 220 nm, this wavelength was used for the following presented electrophrograms.

For quantification, the Mn$^{2+}$ content in the Mn$^{3+}$-standard was determined by the developed CE method. The content of Mn$^{2+}$ in the Mn$^{3+}$-standard was 3.2%, which can be attributed to Mn$^{2+}$-impurities in the Mn(III) acetate salt (97% purity). The amount of Mn$^{2+}$ did not changed after 4 weeks, indicating that the decomposition of Mn$^{3+}$ in the presence of diposphate is very slow.

| Table 1. Relative standard deviations of the peak area and migration time ($n = 10$) and the determined LODs, LOQs, and the linear range of each analyte |
|--------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Stabiliser | Mn$^{3+}$ | Cu$^{2+}$ | Mn$^{2+}$ |
|--------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Peak area (%) | 3.5 | 3.2 | 2.3 |
| Migration time (%) | 0.3 | 0.4 | 0.4 |
| LOD (mg/L) | 0.59 | 0.11 | 0.16 |
| LOQ (mg/L) | 1.83 | 0.35 | 0.52 |
| Linear range (mg/L) | LOQ–50 | LOQ–50 | LOQ–15 |
| $R^2$ | 0.9993 | 0.9998 | 0.9995 |

Samples containing organic carbonate-based electrolytes showed peak shifting to longer migration times increasing with each measurement. Rinsing the capillary with 1 vol% HCl and deionized water before conditioning again with running buffer improved the precision of migration times by reduced peak shifting effects. Nevertheless, the maximum amount of electrolyte in the sample was limited to 1 vol%, because higher electrolyte concentrations led to strongly deformed peaks and migration time shifts.

In the following, the linear range and the reproducibility of the peak areas and the migration times were determined with samples containing 1 vol% electrolyte (Table 1). For reproducibility evidence, 10 mg/L of each standard was measured ten times. The LODs and LOQs were determined by 3σ and 10σ criteria. Unlike the other ions, the linear range for Mn$^{2+}$ was limited to 15 mg/L (Table 1) due to a drop in the slope of the integrated peak area from 15 mg/L upwards, likely caused by lower complex stability.

The recovery rate was determined by dissolving Mn(III) acetate salt in LiIB electrolyte. Besides Mn$^{3+}$, a small amount of Mn$^{2+}$ was detected. This can be attributed to Mn$^{2+}$-impurities in the Mn(III) acetate salt (3.2% Mn$^{2+}$) and to a partly disproportionation reaction of Mn$^{3+}$ due to the some residual water in the Mn(III) acetate salt. In consequence, the sum of the Mn$^{3+}$ and Mn$^{2+}$ concentrations were used for calculation of the recovery rate. The recovery rate was determined to be 103.5 ± 3.1% with a Mn$^{3+}$/Mn$^{2+}$ fraction of 94.1–5.9%, respectively. To rule out disproportionation reac-
tions or reduction of Mn$^{3+}$ during sample preparation due to possible slow complexation, the electrolyte sample was diluted in 27 mM and also in 182 mM diphosphate buffer (pH 3.1) in a volume ratio of 1:5. Afterward, the solutions were diluted with 27 mM diphosphate buffer to a final concentration of 1 vol% electrolyte. No changes in Mn$^{3+}$ and Mn$^{2+}$ concentrations were observed for low and high diphosphate concentrations. Obviously, it can be assumed that the formation of Mn$^{2+}$ took place during sample preparation before buffer addition.

3.2 The effect of a TM-ion-scavenger on the oxidation state of dissolved manganese

TM dissolution has negative effects on LIB lifetime due to the impairment of the SEI. Therefore, some research groups focused on TM-ion-scavengers in LIBs to extend the lifetime. For this, complexing agents were dissolved as additives in the electrolyte or bound to the separator to scavenge-dissolved TM ions from the cathode [22–26]. It is well known that complexing agents can strongly influence the preferred oxidation state of the TM. This phenomenon has particular been considered in speciation analysis, for example, of Fe$^{2+}$ and Fe$^{3+}$. In the absence of the stabilizing ligand 1,10-phenanthroline for Fe$^{3+}$, the species was converted directly to Fe$^{3+}$ in the presence of EDTA by ambient oxygen, hence forming the more stable Fe$^{3+}$–EDTA complex [44]. Li et al. showed the formation of mainly Mn$^{3+}$ in LMO-based cells when using impregnated separators with polymeric aza-15-crown-5 ethers for Mn-scavenging. The investigation of the separator by XANES revealed an average oxidation state of dissolved manganese close to +3 [25].

In this work, diphosphate was used as complexing agent for manganese to stabilize the dissolving Mn$^{3+}$ regarding decomposition and to investigate the possible effect of ion scavengers on the preferred oxidation state of the dissolved manganese. Furthermore, it was demonstrated in previous studies that the dissolution of manganese is strongly accelerated in the presence of acidic compounds as a result of electrolyte decomposition. The effect of the proton concentration was simultaneously investigated with buffered aqueous diphosphate solutions at different pH, which is not feasible with LIB electrolytes. For this, the pH of the solutions was adjusted to 3, 5, and 7 with HCl. Afterward, the synthesized LNMO powder was immersed in the prepared diphosphate solutions. Over 10 weeks, the colorless solutions turned reddish with highest intensities at lower pH values, indicating the formation of Mn$^{3+}$.

Figure 3 shows the electropherogram of a sample stored at pH 5. At 4.5 min (Fig. 3A), NO$_3^-$ from the added Cu$^{2+}$ standard (5 mg/L) migrates, followed by Mn$^{3+}$, Cu$^{2+}$, and finally by Mn$^{2+}$. The overall shifted migration times of the analytes, in comparison to Fig. 1, can be explained by using a new capillary. In comparison to the capillary in this chapter, the used capillary, as shown in Fig. 1, was shortened few centimeters after occurring leak current, leading to slightly faster migration times. In comparison to Mn$^{3+}$, the Mn$^{2+}$ signal (Fig. 3B) was significantly less intense, indicating a minor concentration of Mn$^{2+}$ in the buffer. Figure 4 shows the concentrations of Mn$^{3+}$ and Mn$^{2+}$ of each sample. It is observable that dissolution of manganese occurs even at pH 7. For these
samples, the quantities of Mn$^{3+}$ were below LOQ. Furthermore, it can be noted that the total amount of dissolved manganese (Mn$^{3+}$ and Mn$^{4+}$) increased with lower pH. This was in good agreement with previous results, which reported the accelerated dissolution of manganese under acidic conditions [17, 18, 21, 31, 34, 35]. In contrast to the expected Mn$^{2+}$ from disproportionation reaction, the diphosphate led mainly to the formation of Mn$^{3+}$. The Mn$^{3+}$ fraction of total dissolved manganese in the samples was higher than 98.5% and increased with higher pH. This result corresponds well to the study of Li et al. [25].

The formation of Mn$^{3+}$ can be described in two consecutive steps. In nonstoichiometric LNMO, Mn$^{3+}$ is present in small amounts due to charge compensation of oxygen vacancies in the structure [58, 59]. In a first step, manganese dissolution starts with a disproportionation reaction of surficial Mn$^{3+}$ to soluble Mn$^{2+}$ and Mn$^{4+}$ (Eq. 2) [34]. Then the complexed Mn$^{2+}$ is oxidized to Mn$^{3+}$. Unlike for Fe$^{2+}$ in the presence of EDTA, oxidation of Mn$^{2+}$ in the presence of diphosphate by oxygen was not observed. Therefore, it can be assumed that oxidation of Mn$^{2+}$ took place via a comproportionation reaction of Mn$^{2+}$ with Mn$^{4+}$ at the surface of LNMO particles to trivalent manganese. This reaction involves a one-electron transfer from Mn$^{2+}$ to Mn$^{4+}$. A similar reaction of complexed Mn$^{2+}$ with Mn$^{4+}$ was described by Wang et al. [57]. In this study, the reaction of citrate at the surface of birnessite ($M$,Mn$^{3+/4+}$,O$_2$) was investigated regarding the dissolved manganese species. It was suggested that Mn$^{3+}$-citrate was formed due to the reaction of citrate with birnessite. The complexed Mn$^{2+}$ was then oxidized to Mn$^{3+}$-citrate via a one-electron transfer to the surficial Mn$^{4+}$. By comparing the redox potentials of each half reaction, it was shown that the oxidation of Mn$^{2+}$ to Mn$^{3+}$ is thermodynamically favored. Due to complexation with citrate, the redox potential of complexed Mn$^{2+}$/Mn$^{3+}$ was lowered below the redox potential of Mn$^{2+}$/Mn$^{4+}$ [57]. The complexation with diphosphate led also to a reduced redox potential of Mn$^{2+}$/Mn$^{3+}$, in which most of Mn$^{2+}$ was finally oxidized to Mn$^{3+}$ [56]. The reaction schemes can be summarized as follows:

$$2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+} \quad (2)$$

$$\text{Mn}^{2+}(\text{L})_{\text{aq}} + \text{Mn}^{4+} \rightarrow \text{Mn}^{3+}(\text{L})_{\text{aq}} + \text{Mn}^{3+} \quad (3)$$

As a consequence, the dissolution of Mn$^{2+}$ will generate new Mn$^{3+}$ at the LNMO surface, which then undergoes further disproportionation reactions.

As shown by diphosphate in this work or by the reported polymeric aza-15-crown-5 ether [25], complexing agents can alter the preferred oxidation state of manganese in LIBs. The formation of Mn$^{3+}$ might also occur for other ion-scavenging agents in LIBs and should be subject for further investigations. Additionally, the stability of the ion-scavenging agents can suffer due to the formation of Mn$^{4+}$ as shown for different organic ligands. Therefore, the stability of integrated TM-ion-scavengers in LIBs should be considered in future work [53, 54].

### 3.3 Dissolution of manganese species in organic carbonate-based electrolytes

Common LIB electrolytes are based on conducting salt LiPF$_6$, diluted in different cyclic and linear organic-carbonates [1, 60–62]. Due to the absence of complexing agents in LIB electrolytes, formation of soluble Mn$^{3+}$-species should not be expected. Nevertheless, several studies report on dissolved Mn$^{3+}$ being the main manganese species in common electrolyte in case of the LMO cathode, with abundances of 67–78% after storage and 60–80% after electrochemically treatment in LMO||Graphite cells. For LNMO, the Mn$^{3+}$ amount in the electrolyte after storage was reported to be 12–44% of total dissolved manganese [38, 39].

The dissolution of manganese into electrolyte was performed by immersing LNMO powder into electrolyte. Six samples were stored under water and oxygen-free conditions, three at 20°C and three at 60°C. As observable, only Mn$^{2+}$ was dissolved into the electrolyte (Fig. 5A). These results are contrary to the reported dissolution of Mn$^{3+}$.
into electrolyte, but fits well to findings by Terada et al. [31]. The manganese dissolution already took place at 20°C due to disproportionation reaction and increased with elevated temperatures (Fig. 5B). On the one hand, disproportionation can be accelerated at higher temperatures and, on the other hand, more acidic compounds can be formed at higher temperatures due to accelerated decomposition of the thermal labile conducting salt LiPF₆. Previous studies demonstrated the decomposition of organic carbonates and the conducting salt at elevated temperatures to different acids, like HF or difluorophosphoric acid, especially in the presence of moisture [63–69]. As a consequence, LNMO particles are situated under acidic condition, which was shown to increase the dissolution of manganese [18, 21, 31, 34, 35].

4 Discussion

A CE method for analysis of Mn³⁺ and Mn²⁺ in LIB electrolytes was developed in this study using diphosphate as complexing agent to stabilize both manganese species. Compared to other methods applied on manganese speciation in LIB electrolytes, this method enables a fast and simultaneous detection of Mn²⁺ and Mn³⁺ and also the quantification of both species in a single run. However, other TMs like iron, cobalt or nickel cannot be investigated with this developed method due to instability of some oxidation states in presence of diphosphate or they have not been detected. Dissolution experiments with LNMO powder in buffered aqueous diphosphate solutions at defined pH were performed to investigate the formation of manganese species in the presence of a TM-ion-scavenging agent. These experiments showed mainly the formation of Mn³⁺ with increased concentrations at lower pH, which was in line with previous reported results [17, 18, 21, 31, 34, 35]. Also, the formation of mainly Mn⁴⁺ was in good agreement to a study, in which polymeric aza-15-crown-5 ethers were used for Mn-ion-scavenging in LMO-cells [25]. It can be assumed that the formation of Mn³⁺ took place in two steps: (1) dissolution of Mn²⁺ from LNMO via disproportionation reaction and (2) oxidation of complexed Mn²⁺ via one electron transfer by Mn⁴⁺ at the LNMO surface. In comparison, storage experiments of LNMO in LIB electrolyte at defined temperatures did not show any formation of Mn⁴⁺, solely of Mn³⁺. Furthermore, the dissolution of Mn³⁺ was accelerated at elevated temperatures due to the decomposition of the electrolyte. The absence of Mn¹⁺ is contrary to those studies, which reported dissolution of Mn³⁺ and Mn⁴⁺ from LMO or LNMO cathode materials into LIB electrolytes [38, 39].

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