Fe and Co methylenediphosphonates as conversion materials for Li-ion batteries

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Abstract

Organic-inorganic hybrid materials can introduce more flexibility in the choice of Li-ion battery materials due to the versatility of organic ligands. As an alternative to carboxylate-based ligands, Fe and Co methylene diphosphonate were successfully synthesised and tested as model diphosphonate-based negative electrode materials for Li-ion batteries, showing specific charges of 250 mAh g⁻¹ and 395 mAh g⁻¹ after 100 cycles at 50 mAh g⁻¹, respectively. *Operando* X-ray diffraction and *ex situ* X-ray absorption spectroscopy confirmed the expected conversion reaction mechanism involving amorphisation of the pristine materials and extrusion of transition metal particles upon reduction. *Ex situ* X-ray absorption spectra indicated that Fe methylene diphosphonate undergoes reversible Fe cycling between Fe(II) and Fe(0) metal particles.

1 Introduction

Portable electronic devices and new-generation hybrid and fully electric vehicles use Li-ion batteries as a power supply because these batteries currently provide the highest energy density. Increased consumer demand for higher energy autonomy of their devices, especially for vehicles, requires an increase in the energy density of batteries. In order to fulfil this goal, different classes of materials capable of storing more electrical energy have been investigated. Besides the intensively studied positive electrode materials, transition metal oxides, phosphates, and silicates [1], as well as alloy/conversion materials for negative electrodes [2], other new electrode materials are receiving increased attention, exemplified by the use of organic-inorganic hybrid electrode materials [3]. The advantage of organic-inorganic hybrids is their tunable organic part, which gives rise to a wide choice of synthetic possibilities. Metal-organic frameworks (MOFs) are the most reported class of hybrid organic-inorganic materials used in Li-ion batteries. Typically, the organic materials are linked to metal ions by carboxylate functional groups, exemplified by benzenedicarboxylate used in MIL-53 and MIL-68 by Férey et al. [4, 5], or oxalate used in the oxalatophosphates reported by Nagarathinam et al. and Shahul Hameed et al. [6, 7]. Only few examples of active organic-inorganic hybrid materials with other ligands are described, e.g. Fernandez de Luis et al. used bipyridine ligands to form brannerite-type structures as negative electrodes for the conversion reaction in Li and Na-ion batteries [8]. The authors reported a specific charge of 300 mAh g⁻¹ for Na half-cells after 25 cycles, but did not take the specific charge contribution of the carbon black additive (27 wt.%) into account,

and the long-term cycling properties remain unknown so far. To the best of our knowledge, no experimental proof of the extrusion of transition metal nanoparticles has yet been reported for conversion-reaction hybrid materials, therefore a definite proof of the assumed conversion reaction mechanism was never provided so far. Lin et al. [9] reported a Zn-imidazole-2-aminobenzimidazole bifunctionalised MOF with a specific charge of 225 mAh g^{-1} , when cycled between 0.01–3.0 V vs. Li^+/Li . The structure remains stable after 200 cycles, as shown by *ex situ* X-ray diffraction (XRD). Once again, the contribution of the carbon black was unfortunately not taken into account. Similar results were obtained by An et al. using a Ni-tetramethylbipyrazole MOF, which provides a stable specific charge of 120 mAh g^{-1} after 100 cycles, when cycled between 0.01–3.0 V [10]. The presence of the pristine structure after 100 cycles was demonstrated by *ex situ* XRD.

Recently, we reported the use of lithium iron methylenediphosphonate (FeMeDP) as a positive electrode material [11], which exhibited stable behaviour over more than 200 cycles. Pramanik et al. demonstrated the possibility of using iron phosphonate for negative electrodes of Li-ion batteries [12], with a relatively stable specific charge maintained at 355 mAh g^{-1} after 30 cycles between 0.01–2.0 V vs. Li^+/Li . Once again, no investigation of the reaction mechanism was provided. Xu et al. demonstrated that $\text{Li}_2\text{FeSiO}_4$, which is generally used as positive electrode material, can also be used as negative electrode following a conversion reaction mechanism [13]. Therefore, we decided to investigate the electrochemical properties of metal methylene diphosphonates (Fe (FeMeDP) and Co (CoMeDP)) as model systems for transition metal diphosphonates and to determine the reaction mechanism when they are cycled as negative electrodes at potentials below 3 V vs. Li^+/Li .

2 Experimental

Transition metal methylene diphosphonates were obtained using an established hydrothermal procedure described elsewhere [11]: CoMeDP ($\text{Li}_{0.5}\text{Co}_{1.75}[\text{CH}_2(\text{PO}_3)_2]\cdot\text{H}_2\text{O}$) and FeMeDP ($\text{Li}_{0.2}\text{Fe}_{1.7}[\text{CH}_2(\text{PO}_3)_{1.75}(\text{PO}_3\text{H})_{0.25}]\cdot\text{H}_2\text{O}$) were prepared from the corresponding metal precursor, tetraethyl methylenediphosphonate (98%, Alfa Aesar), and LiOH (98%, Sigma Aldrich). The metal precursors used were $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (99%, Sigma Aldrich) and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (98%, Alfa Aesar). Here, oxalic acid was used instead of ascorbic acid for controlling the pH. X-ray powder diffraction analysis (XRD) was performed at room temperature on a PANalytical Empyrean diffractometer with a $\text{Cu } K_\alpha$ radiation source. Neutron diffraction was measured at the HRPT beamline at the Swiss Spallation Neutron Source SINQ using a wavelength of $1.886 \text{ \AA}$. Scanning electron microscopy (SEM) was performed on a Zeiss Ultra55 SmartSEM electron microscope.

Crystal structure refinement was performed by FullProf 3.00 software using the Rietveld refinement method [14].

Operando X-ray powder diffraction spectra were recorded at room temperature on a PANalytical Empyrean diffractometer with $\text{Cu } K_\alpha$ radiation using an in-house developed electrochemical cell [15] with a beryllium window.

Electrochemical experiments were performed in coin-cell type electrochemical cells, cycled at 50 mA g^{-1} with a 5 h potential hold after each half-cycle (constant current/constant voltage, CC/CV) to ensure complete reduction and oxidation of the materials. Details of electrode formulation and the electrochemical measurement protocol for *ex situ* and *operando* experiments can be found in the

supporting information. Due to the structural changes occurring upon reduction below 1.5 V vs. Li^+/Li , cyclic voltammetry measurements were performed in two potential windows, first between 1.5–4.9 V vs. Li^+/Li for 5 cycles, then between 0.1–3.0 V vs. Li^+/Li for 5 other cycles. All potentials referred to in the manuscript are measured vs. Li^+/Li .

Ex situ X-ray absorption (XAS) was measured at the SuperXAS beamline at the Swiss Light Source, PSI, Switzerland at the Fe K-edge (using a Si(111) channel-cut monochromator [16] in transmission mode with N_2 -filled ionization chambers and by measuring the spectra of Fe metal foils simultaneously as absolute reference. After energy calibration based on the measured reference and averaging of the recorded spectra, the XAS data were analysed using the Demeter © software package, version 0.9.24 [17]. For the EXAFS fitting procedure, the spectra were background-corrected and normalized, after which the energy units (eV) were converted to photoelectron wave vector k units ($\text{\AA}^{-1}$) by assigning the photoelectron energy origin, E_0 , corresponding to $k = 0$, to the first inflection point of the absorption edge. The resulting $\chi(k)$ functions were weighted with k^2 to compensate for the dampening of the XAFS amplitude with increasing k . The resulting k^2 -weighted spectra were Fourier-transformed in a window of 3–11 $\text{\AA}^{-1}$. The fully reduced sample was fitted in the Fourier transformed EXAFS in the range of 1.4–2.9 $\text{\AA}$ using the first Fe-Fe scattering path from a Feff calculation based on the α -Fe crystal structure (ICSD #180971, [18]). The fully oxidized sample was fitted in a window of 1–2.9 $\text{\AA}$ in the Fourier-transformed spectra using three scattering paths (Fe-O, Fe-P and Fe-Fe based on reasonable average values of the corresponding paths calculated from the crystal structure of pristine lithium iron methylenediphosphonate [11]), where all parameters were allowed to run free, as due to the amorphisation it was not clear if the interatomic distances of FeMeDP would be preserved. The sample after the first oxidation potential plateau was fitted in the range of 1.2–2.9 $\text{\AA}$ in the Fourier-transformed spectra using two scattering paths (Fe-O and Fe-Fe). For all fits, the amplitude reduction factor S_0^2 , factor was fixed to the value (0.60) determined from fitting the Fe reference foil and the mean-square displacement factors σ^2 were fitted as independent parameters for all paths.

3 Results and Discussion

FeMeDP and CoMeDP were successfully synthesised by a slight variation of the previously described synthetic method [11]. Oxalic acid was used instead of ascorbic acid to increase the crystallinity of the final products. Similar to FeMeDP, CoMeDP adopts a platelet-like shape with ca. 1 μm diameter and ca. 90 nm thickness (Figure 1B). It can be seen from X-ray diffraction results that CoMeDP has a crystal structure similar to that of FeMeDP [11] and the one reported by Lohse and Sevov [19]. The diffraction peaks are shifted to higher 2θ angles compared to FeMeDP, indicating slightly smaller unit cell parameters (Figure 1A). This observation was partially confirmed by a Rietveld refinement based on neutron powder diffraction data (Table 1): the b and c lattice parameters are smaller, lattice parameter a however was found to be larger for CoMeDP. Still, it corresponds to an overall shrinkage of the unit cell volume. Unfortunately, CoMeDP always contains an undefined impurity phase (unassignable to any reasonable phase in the pdf database) that impairs the refinement quality, since the impurity main peak region is excluded from the fit. The plot of the structural refinement can be found in the supporting information (Figure S1).

Figure 1. A: X-ray diffraction patterns of FeMeDP and CoMeDP. B: SEM images of CoMeDP. C: refined crystal structure of CoMeDP. The blue polyhedra depict CoO_4 and CoO_6 , the grey tetrahedra PO_3C , the red atoms O, the black atoms C, the rose pink atoms H and the teal atoms Li.

Table 1 Unit cell parameters of CoMeDP as refined based on powder neutron diffraction data compared to the unit cell parameters of FeMeDP from [11].

	a [Å]	b [Å]	c [Å]	β [°]	v [Å ³]
CoMeDP	18.8319(7)	8.2641(3)	8.9255(3)	106.669(3)	1330.70(9)
FeMeDP [11]	18.7900(7)	8.3125(3)	8.9587(3)	107.085(1)	1337.52(9)

Cyclic voltammetry measurements were performed for both materials in two potential windows, 1.5–4.9 V and 0.1–3.0 V. In the 1.5–4.9 V potential window, the profile is dominated by a large anodic peak between 4.6–4.9 V, attributed to electrolyte decomposition [20]. In addition to this feature, it

can be seen that CoMeDP is hardly electrochemically active in this potential range, whereas FeMeDP shows some reversible electrochemical activity between 2.0–4.0 V (Figure 2A, B), corresponding to the reversible reduction/oxidation of the Fe(III)/Fe(II) redox couple [11].

When FeMeDP and CoMeDP are reduced to 0.1 V (Figure 2C, D), they both show intense peaks in the first reduction at 0.42 V and 0.63 V, respectively (Figure 2C). This observation is attributed to a conversion reaction mechanism involving the extrusion of the transition metal(II) as nanoparticles, as described by Poizot et al. for metal oxides [21] and subsequently found for various transition metal pnictides, chalcogenides and fluorides [22]. The shoulder at 0.8 V for FeMeDP is attributed to the formation of the solid electrolyte interphase (SEI) by electrolyte reduction in analogy to previous reports [23], which for CoMeDP coincides with the metal reduction peak and is therefore not visible as distinct feature. During the first oxidation, FeMeDP shows one broad anodic peak at 1.10 V, consisting of (at least) two overlapping peaks. CoMeDP shows two distinct anodic peaks: a minor one at 1.02 V and a major one at 1.35 V. Additionally, there is a broad anodic peak observed for both materials between 2.0–2.8 V. In the following cycles (Figure 2D), two reduction peaks are observed for Co (1.78 V and 0.81 V) and Fe (1.35 V and 0.56 V). For the corresponding oxidations, two peaks can also be observed at 1.02 V and 1.34 V for Co and at 1.06 V for Fe (with a shoulder at 1.25 V), and the broad peak above 2 V for both materials (Figure 2D). This behaviour supports the assumed conversion mechanism, since a distinctly different potential profile is observed after the first (irreversible) cycle, indicating a completely different cycling mechanism. However, the reaction mechanism with the oxidation and reduction occurring both in two distinct potential ranges is different compared to the well-studied Fe oxide [24–26] and Co oxide [27, 28] conversion materials, which especially in reduction show only one electroactive potential region in CV. This demonstrates that the organic MeDP ligand has an influence on the assumed conversion mechanism of FeMeDP and CoMeDP. The precise role of the MeDP ligand is currently under investigation and will be the focus of a future publication.

As the profile still exhibits slight changes between the 2nd and the 4th cycle (Figure 2D), e.g. the reduction peak for FeMeDP at 1.35 V is getting narrower; a further slight evolution of the reaction mechanism is taking place upon cycling. The weak reduction peak at 0.87 V present in the 2nd cycle reduction of FeMeDP but disappearing in the following cycles is attributed to electrolyte reduction due to an insufficient passivation layer after the 1st cycle.

Figure 2. Cyclic voltammograms of FeMeDP and CoMeDP. **A:** 1st cycle between 1.5–4.9 V. **B:** 2nd and 4th cycles between 1.5–4.9 V. **C:** 1st cycle between 0.1–3.0 V. **D:** 2nd and 4th cycles between 0.1–3.0 V. The contribution of the carbon black conductive additive in the low-potential region is indicated by the blue cyclic voltammogram.

Based on these results, CC/CV cycling tests were performed to investigate long-term electrochemical properties of FeMeDP and CoMeDP (Figure 3). The 1st cycles show high irreversibility (42% for FeMeDP and 34% for CoMeDP) and a high specific charge of 970 mAh g⁻¹ and 805 mAh g⁻¹ for the reduction of FeMeDP and CoMeDP, respectively. The low coulombic efficiency of the first reduction is a further indication of a conversion-type mechanism [21, 22]. Note that the carbon black additive contributes ca. 170 mAh g⁻¹ to the specific charge (420 mAh g⁻¹ for the 1st reduction), which was not subtracted in the figures, but from the indicated values. The contribution was determined by cycling only carbon black in the corresponding potential window and multiplying the obtained specific charge by the diphosphonate-to-carbon black ratio in the diphosphonate electrodes, i.e. 80% (Figure S2). In the following cycles, the irreversibility and specific charge decrease rapidly, in agreement with the assumed conversion reaction mechanism. After 50 cycles, the specific charge for both materials is close to 250 mAh/g (FeMeDP 220 mAh g⁻¹, CoMeDP 265 mAh g⁻¹). Interestingly, the specific charge increases by approx. 0.6 mAh g⁻¹ and 2.6 mAh g⁻¹ per cycle after 50 cycles to reach values of 250 mAh g⁻¹ and 395 mAh g⁻¹ for the 100th cycle of FeMeDP and CoMeDP, respectively (Figure 3).

Figure 3. Evolution of specific charge for FeMeDP and CoMeDP cycled at 50 mA g⁻¹ between 0.1 – 3.0 V.

It is important to note that a conversion reaction mechanism involving only the M(II)/M(0) redox couple should deliver a specific charge of ca. 336 mAh g⁻¹. The higher specific charge obtained for CoMeDP supposedly originates from interfacial charging, as modelled by Zhukovskii et al. [29], even if a possible contribution of the organic ligand cannot be fully excluded at this stage [30].

To assess the rate capability of FeMeDP and CoMeDP, both materials were cycled without potentiostatic step at increasing rates between 50 – 1000 mA/g (Figure S3). For both materials, a similar rate capability was found (see supporting information).

The galvanostatic curves were studied to clarify the conversion reaction mechanism and the possible activation that occurs for long-term cycling. During the 1st reduction, FeMeDP and CoMeDP show a rapid potential drop followed from open circuit voltage (OCV) to 0.80 V and 1.01 V, respectively, where a long potential plateau appears (Figure 4A, B). The cathodic plateau of FeMeDP accounts for approximately half of the total specific charge of the first reduction, while the first potential plateau of CoMeDP only contributes ca. 35% of its total specific charge. However, CoMeDP exhibits a second cathodic plateau at 0.80 V, with the combination of the two plateaus at 1.1 V and 0.80 V corresponding to ca. 55% of the total specific charge of its 1st reduction. For both materials, a large irreversible specific charge is thereby recorded (Figures 3, S4, and S5). The potential plateaus of both materials are attributed to i) the formation of the solid electrolyte interphase (SEI) [23] and ii) the reduction of the materials upon extrusion of transition metal particles.

In the 1st oxidation, FeMeDP and CoMeDP exhibit potential plateaus at 1.0 V and 1.22 V, respectively (Figure 4A, B), where we expected the (partial) reoxidation of transition metal ions to occur, accompanied by the formation of Fe–O bonds. For CoMeDP, an additional, small plateau at 0.95 V can be observed, as expected from the CV results. Additionally, a sloping potential region between 2.0–2.5 V is detected for both materials, where the metals are fully reoxidised (see next paragraph on XAS).

In accordance with the two peaks observed in the CV curves, the second reduction also features two sloping potential plateaus for both materials, showing that a corresponding reduction exists for both oxidation plateau regions (Figure 4A, B). The above indicates that the oxidation and reduction reaction pathways after the first conversion are similar. The different behaviour in the 1st reduction is due to the fact that upon oxidation, the initial particle size and morphology is not reformed for

conversion materials leading to a larger influence of surface reactions compared to the bulk, as described by Cabana et al. [22]

The following cycles exhibit a slow evolution of the galvanostatic profile: in addition to increasing polarization, which we attribute to a growing passivation layer, the upper potential regions for oxidation and reduction decrease in length up to the 50th cycle, indicating that the reaction taking place at high potential is the main source of specific charge fading (Figure 4A, B). After the 50th cycle, i.e. when the specific charge starts to increase, the potential profile also changes. This can be better observed for the derivatives of galvanostatic curves (dQ/dU) (Figure 4C,D). A new weak cathodic peak appears for FeMeDP at 0.95 V, which grows and shifts to higher potentials, reaching 1.07 V in the 100th cycle (Figure 4C). Upon oxidation, the broad area between 1.25-2.25 V is slightly enhanced, with a similar effect observed for CoMeDP (Figure 4D). From the changes in the potential profile, we assume that it originates from a new reaction pathway occurring parallel to ageing which is responsible for the increasing specific charge after 50 cycles.

Figure 4. **A:** Normalized CC/CV profile of FeMeDP. **B:** Normalized CC/CV profile of CoMeDP. **C:** Derivative of the galvanostatic profile of FeMeDP. **D:** Derivative of the galvanostatic profile of CoMeDP. For all figures, the materials were cycled at 50 mA g⁻¹ between 0.1 V–3.0 V.

Operando X-ray diffraction (XRD) and *ex situ* X-ray absorption (XAS) spectra were recorded for FeMeDP. XRD results showed that the pristine structure is irreversibly amorphised during the 1st reduction, and no new crystalline phase can be detected (Figure S6). The X-ray absorption near-edge

structure (XANES) spectra collected at the Fe K-edge demonstrate a mostly reversible shift from Fe(II) in the pristine material to Fe(0) in the fully lithiated material, validating the conversion reaction mechanism that involves extrusion of Fe(0) nanoparticles during reduction below 0.8 V (Figure 5B, C). From the extended X-ray absorption fine structure (EXAFS) spectra, a reversible shift of the nearest-neighbour distances from smaller (corresponding to Fe–O bonds in the pristine material) to larger values (attributable to Fe–Fe bonds in the reduced material) could be observed (Figure 5D). The EXAFS spectrum of the fully reduced material (0.1 V) could be fitted by the crystal structure of α -Fe with good accuracy (Table S1). The obtained Fe–Fe distance of 2.45 ± 0.01 Å is in good agreement with the corresponding value of 2.46 ± 0.01 Å fitted for the Fe reference foil (Figure S8, Table S1). In addition, the assumed formation of nanosized particles is supported by the absence of higher-shell scattering paths: when the second Feff-calculated Fe–Fe path was added to the fit, the obtained coordination number was 0.0 ± 1.3 , for the final fit it was therefore omitted.

At full reoxidation (3.0 V) (Figure 5D), it is important to note that the shape of the first-shell peak is not exactly the same as for the pristine material, but very similar to the measurement taken before the long potential plateau (0.8 V), it can also be observed from the corresponding XANES spectra (Figure S7). Therefore, the initial reduction is not completely reversible. The nearest-neighbours of the reoxidised (3.0 V) FeMeDP sample could be best fitted using three different scattering paths (Table S1): Fe–O at a distance of 2.01 ± 0.01 Å, Fe–P at a distance of 2.84 ± 0.03 Å, and Fe–Fe at a distance of 2.51 ± 0.02 Å. This path has to originate from residual metallic Fe, as for FeMeDP the shortest Fe–Fe distance would be 3.23 Å, for lithium iron phosphate as another typical example even 3.90 Å. This Fe-nearest neighbour still has a coordination number of 1.5 ± 0.5 (Figure S9, Table S1). Compared to the fitted coordination number of 6.1 ± 0.5 for the fully reduced material, this shows that an approximate 25% of the Fe has not been reoxidised.

These findings match the proposed conversion reaction mechanism. The difference between the pristine and the fully reoxidised material also agrees with the XRD data, both results indicate that the initial crystal structure is not reformed. After the first oxidation plateau (1.28 V), Fe is partially oxidized, and some Fe–O bonds are reformed, however, only as a minor contribution (coordination number of 0.3 ± 0.2) (Table S1). This is surprising, since it relativizes our hypothesis of metal oxidation during the first long oxidation plateau. Undoubtedly, Fe is oxidized to some extent, but the low Fe–O contribution and the weak edge shift compared to the length of the potential plateau (ca. 280 mAh g⁻¹, i.e. over 80% of the theoretical specific charge for a two-electron oxidation of all Fe present) indicate the occurrence of another process in this potential range, in addition to Fe oxidation. Iron is further oxidized in the more sloping region that follows the plateau. A possible additional mechanism could involve the reoxidation of diphosphonate ligands reduced either in the conversion potential plateau or in the adjacent sloping region. This hypothesis is the focus of the aforementioned investigation on the ligand influence on the conversion mechanism.

Figure 5. XAS measurements of FeMeDP. **A:** Potential profile of the 1st cycle for FeMeDP, with arrows indicating the potentials at which *ex situ* XAS was measured. **B:** Normalized XANES spectra of Fe methylene diphosphonate cyclized to different states of charge during reduction. **C:** Normalized XANES spectra of Fe methylene diphosphonate cyclized to different states of charge during reoxidation, with the pristine spectrum shown for comparison. **D:** R-space representation of the EXAFS spectra analysis for different states of charge for Fe methylene diphosphonate. The spectra of samples being reoxidised (1.28 V and 3.0 V) are depicted by dashed lines. In all figures, the spectra of Fe metal and FeSO₄·7H₂O (as Fe(0) and Fe(II) references) are shown in dotted lines.

4 Conclusion

The effectiveness of transition metal diphosphonates as conversion materials in Li-ion batteries was demonstrated by cyclic voltammetry and galvanostatic cycling of the model materials FeMeDP and CoMeDP. These materials show a stable specific charge of ca. 230 mAh g⁻¹ and 265 mAh g⁻¹ (corrected values taking into account the contribution of the carbon black additive), respectively, when cycled between 0.1–3.0 V at 50 mA g⁻¹. Interestingly, the specific charge continuously increases even after the 50th cycle, reaching values of 250 mAh g⁻¹ and 395 mAh g⁻¹ after 100 cycles for FeMeDP and CoMeDP, respectively. We demonstrated that the hybrid transition metal diphosphonate materials follow a conversion reaction mechanism using *operando* XRD and *ex situ* XAS. To the best of our knowledge, we provide a first-time experimental confirmation of the extrusion of transition metal particles upon reduction of an organic-inorganic hybrid material.

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