The thesis document includes the following changes in answer to the external review process.

I am grateful to the Jury Members for their positive feedback and useful comments. I am happy to address the comments and questions in this document and in the revised version of the Thesis. I would also like to note that I updated the Acknowledgements section and the list of publications, which now includes a manuscript that was submitted after the reviews from the Jury Members had been received.

Response to Prof. Evgeniy Antipov

From my point of view, the statement in Literature review on p. 55 that “From general considerations, Ni(I) is an exotic state for nickel that typically exists only in elusive intermediate states” is wrong because a few compounds containing Ni(I) based on LaNiO2 structure and etc. have been intensively studied recently because they exhibit superconductivity at low temperatures up to 15K.

The passage about the rarity/instability of Ni(I) was removed from the Literature review in its revised version. This did not influence the general message about the data presented in ref. 129 and interpretation of these data by the authors. I would like to note that after the Thesis was submitted, the investigation of charge storage mechanisms for NiTIB was continued. Particularly, we studied the behavior of NiTIB at the potentials below 0.5 V vs. M+/M (M= Li, Na or K), as attempted by the authors of ref. 129 for the Na-based cells. Together with Prof. Andriy Zhugayevych we collected evidence that after the two-electron reduction of the ligands takes place, no further reduction of the material occurs even at ~0 V vs. M+/M. If needed, I would be happy to discuss these new results during the Q&A session at the Thesis defense.

1) On page 57 “To test the ball-milled polymers as cathode materials, active materials, Super P carbon black and poly(vinylidene difluoride) (PVdF) with the mass ratio of 4:5:1 were thoroughly mixed with N-methylpyrrolidone (NMP) to form a homogeneous slurry”. Why such a low fraction of the active material was used?

When evaluating the electrochemical performance, it is a common practice for organic-based materials to start with low contents of active materials and low areal capacities (see, for example, Peng et al., Nat. Energy 2017, 2, 17074; Dong et al., Nat. Energy 2020, 5, 1043-1050; Patil et al., Adv. Mater. 2017, 29, 1703373; Tang et al., J. Mater. Chem. A 2019, 7, 486-492). It is known that the battery performance depends on numerous parameters, such as electrode architecture, content of conductive fillers, areal loading, etc. At the initial stage of the material development, it might be useful to assess their performance in loose conditions, i.e., in diluted thin electrodes. It helps to estimate the intrinsic limits of the materials rather than analyze the properties of unoptimized electrodes for which it might be challenging to identify the key factors affecting the performance. Investing resources into further electrode design (which can take months or even years) is justified only when the active electrode materials have intrinsically attractive properties.
During my PhD studies, the initial electrochemical tests were performed with diluted thin electrodes. This initial round of tests showed that NiTIB had promising features as an anode material. At the same time, NiTIB had modest characteristics as a cathode material. Likewise, the moderate performance of CuTIB showed that it would be uncompetitive from the practical perspective. Considering these results, I decided to focus on NiTIB as the anode material. This included the first steps of electrode design (decreasing the carbon content, varying the areal capacity) as well as in-depth investigation of charge storage mechanisms. At the same time, the research on CuTIB, as well as NiTIB as the cathode material, was halted, so no optimization of the electrode composition was carried out.

Since decent performance was achieved for NiTIB-based anodes with low carbon contents (10-15 wt. %), the data for the diluted electrodes were redundant (because they are less strict and farther from the industrial standards) and were not included to the Thesis for this reason. In the revised version of the Thesis (section 5.3.1, p. 79), I added a note that the performance of NiTIB was evaluated in the diluted electrodes as well; I also provided a reference to our paper where these data can be found.

2) Why the Cu-based polymer was amorphous while the Ni-based one was prepared in the crystalline form? Did the author make attempts to synthesize this polymer at other synthesis conditions?

It might be supposed that the copper-based material is disordered because, in contrast to NiTIB, its formation involves reduction of metal ions by benzenetetramine, which is evidenced by presence of Cu$_2$O in the sample. This side reaction possibly results in a different structure of CuTIB intermediates, as well as increased concentration of defects that prevents long-range ordering. Since a part of Cu$^{2+}$ is consumed by Cu$_2$O precipitation, it results in off-stoichiometry between the ligands and the metal ions, which leads to decreased polymerization degree due to chain termination by the ligand moieties. It was previously shown that such off-stoichiometry leads to amorphization of similar coordination polymers (Park et al., J. Am. Chem. Soc. 2018, 140, 10315-10323).

Although no optimization studies have been performed for CuTIB yet, I agree that synthetic conditions might strongly affect the crystallinity and purity of the resulting material. For example, crystallinity of a Cu-based MOF derived from hexaaminobenzene improves when a supporting ligand, ethylenediamine, is added and the solvent is tuned to slow down nucleation (Park et al., J. Am. Chem. Soc. 2018, 140, 10315-10323). It might be supposed that similar strategy can be applied to obtain the crystalline CuTIB. Cu$^{2+}$ reduction can be suppressed by increasing the redox potential of copper ions (via changing their coordination environment). Alternatively, benzenetetramine can be oxidized into 2,5-diamino-1,4-benzoquinonedimine (Audi et al., Chem. Commun. 2014, 50, 15140-15143) before Cu$^{2+}$ ions are introduced into the reaction mixture. Discussion of this issue was expanded in the revised version of the Thesis, section 5.1, p. 67.

3) To my mind the estimation of specific energy for these materials (like as 616 Wh/kg for CuTIB) is very speculative because anions from the electrolyte are not taken into account as it was written in the thesis “...the positive charge on the polymer backbone was balanced by PF$_6^-$ anions”.

To circumvent this bias with the specific energy, its discussion was expanded in the revised version of the Thesis, section 5.2.1, pp. 73-75. Particularly, I estimated the specific energies considering the masses of counter-ions required for the battery operation. Although in my experiments LiPF$_6$ originated solely from the electrolyte, it is principally possible to use mixtures of solid salts and relatively small amounts of electrolyte (Yang et al., Nature 2019, 569, 245-250). For this reason, the total mass of the electrolyte was not considered.

4) Did the author try to carry out a chemical analysis of the sodiated and potassiated polymers?

The sodiated and potassiated materials were studied with a set of techniques, including operando and ex situ X-ray diffraction and Raman spectroscopy. The potassiated structure was investigated with ex situ X-ray photoelectron spectroscopy and UV-Vis-NIR spectroscopy. The data are available in section 5.3.2.

Response to Prof. Stanislav Fedotov

1. There are some inconsistencies in the literature overview to be corrected.
   a. P. 33 in the capacity definition, “structural unit” is not a correct term. It is better to use “formula unit”.

The term “structural unit” was corrected to “formula unit”.
b. In p. 35 dendrites normally form at charging, not discharging.

The phrase “making fast charging-discharging of the batteries safe” was corrected to “making fast charging of the batteries safe”.

c. P. 40 KF and KHCOO solutions are not neutral, but basic due to hydrolysis.

The phrase “redox features of NiHIB were present only with basic solutions, while rectangular-shaped CV profiles were observed with neutral electrolytes, e.g., KF, KBr or KHCOO solutions” was corrected to “redox features of NiHIB were present only with strong alkaline solutions (such as 0.5–1 M KOH), while rectangular-shaped CV profiles were observed with neutral or mildly basic electrolytes, e.g., KF, KBr or KHCOO solutions”.

2. Why for the synthesis of NiTIB a chloride was taken, but for CuTIB – sulfate, not chloride? Could the anion influence the crystallinity of the CuTIB material?

Crystallinity of CuTIB is poor with both aq. CuSO₄ and aq. CuCl₂ as reagents. Brief discussion about it was added to the Thesis, section 5.1, p. 67, and the XRD data were added to Appendix A, Figure A3. Such result was expectable because both sulfate and chloride are stable cations that should not strongly coordinate metal ions or undergo redox reactions under given conditions. Additionally, no sulfur or chlorine were found in the resulting materials by the elemental analysis, as indicated in section 5.1, meaning that the anions do not form side products in detectable quantities.

The copper-based material is likely disordered because, in contrast to NiTIB, its formation involves reduction of metal ions by benzentetramine, which is evidenced by presence of Cu₂O in the sample. This side reaction possibly results in a different structure of CuTIB intermediates, as well as increased concentration of defects that prevents long-range ordering. Since a part of Cu^{2+} is consumed by Cu₂O precipitation, it results in off-stoichiometry between the ligands and the metal ions, which leads to decreased polymerization degree due to chain termination by the ligand moieties. It was previously shown that such off-stoichiometry leads to amorphization of similar coordination polymers (Park et al., J. Am. Chem. Soc. 2018, 140, 10315-10323). Discussion of this issue was expanded in the revised version of the Thesis, section 5.1, p. 67.

3. For the tests as cathodes the electrode composition was 4:5:1, while for anode tests – 8:1:1. What was the reason for such a low fraction of active material in case of cathodes? And what is the general idea to change the composition depending on the electrode potential window?

During my PhD studies, all initial electrochemical tests (for both materials and for both cathode and anode applications) were performed with thin electrodes containing 50% wt. of carbon. Starting with high contents of carbon is a common practice for organic-based materials (see, for example, Peng et al., Nat. Energy 2017, 2, 17074; Dong et al., Nat. Energy 2020, 5, 1043-1050; Patil et al., Adv. Mater. 2017, 29, 1703373; Tang et al., J. Mater. Chem. A 2019, 7, 486-492), and it helps estimate intrinsic limits of the materials in loose conditions. The initial round of tests showed that NiTIB had promising features as an anode material. At the same time, NiTIB had modest characteristics as a cathode material. Likewise, the moderate performance of CuTIB showed that it would be uncompetitive from the practical perspective. Considering these results, I decided to focus on NiTIB as the anode material, which included the first steps of electrode design (decreasing the carbon content, varying the areal capacity). No such work was done for CuTIB, as well as for NiTIB as the cathode material – it was assumed that if the materials show moderate characteristics in loose conditions, the performance should be even worse with lower carbon contents.

Fortunately, decent performance was achieved for NiTIB-based anodes with low carbon contents (10-15 wt.%). At this point, the data for the diluted electrodes were redundant (because they are less strict and farther from the industrial standards) and were not included to the Thesis for this reason. In the revised version of the Thesis (section 5.3.1, p. 79), I added a note that the performance of NiTIB was evaluated in the diluted electrodes as well; I also provided a reference to our paper where these data can be found.

4. When measuring ionic conductivity for coordination polymers did you deposit electron conducting electrodes onto the pellet sides? What was the applied pressure to form a pellet?
Initially, there were no conductive electrodes deposited onto the pellets prior to the conductivity measurements. During the revisions, I remeasured the electron conductivity of both materials with a more precise instrument (BioLogic VMP3 instead of Elins P-45X) using DC polarization. For these measurements, I coated top and bottom of the pellets with gold using magnetron sputtering. The details were added to the Experimental section. Updated values for the electron conductivities at room temperature are 2.0*10^{-7} S cm^{-1} for NiTIB and <10^{-13} S cm^{-1} for CuTIB (direct current was <10^{-13} A cm^{-1} when the voltage was set to 2 V). This information was added to the revised version of the Thesis, section 5.1, pp. 69-70.

For making the pellets, the applied load was 5 metric tons, the pellet diameter was 10 mm. This information was added to the Experimental section.

5. The reasoning of choosing specific electrolytes (solvents and salt concentrations) for different metal systems should be elucidated.

1 M LiPF₆ in EC:DMC was selected because it is a standard commercially available electrolyte for Li-ion batteries that is used in the industry (Xu, Chem. Rev. 2004, 104, 4303-4418). 1 M LiTFSI in DME:DOL was selected because it is one of the most widely applied ether-based electrolytes; for example, it is a standard electrolyte for Li-S cells (Zhang, J. Power Sources 2013, 231, 153-162). 1.5 M NaPF₆ and 1.5 M KPF₆ in DME were selected as electrolytes for sodium- and potassium-based cells, respectively, because decent results were achieved with these electrolytes for other organic-based materials (Kapaev et al., ACS Appl. Energy Mater. 2021, 4, 4465-4472; Kapaev et al., ACS Appl. Energy Mater. 2021, 4, 10423-10427). It was assumed that 1.5 M concentration was better than 1 M because it should increase the ionic conductivity (Qin et al., Adv. Energy Mater. 2019, 9, 1902618). DME was selected because of its low viscosity that also should improve the conductivity. A brief discussion about the electrolytes was added to the revised version of the Thesis, section 5.2.1, p. 71, and section 5.3.1, p. 78 and p. 79. No thorough research dedicated to the optimization of the electrolytes has been performed for NiTIB/CuTIB yet. This is a subject of future studies.

6. What are the n numbers in the formula for NiTIB and CuTIB?

Unfortunately, determination of the polymerization degree of is challenging for NiTIB and CuTIB. Chromatographic methods, such as GPC, are inapplicable for these materials because they are insoluble in water or organic solvents (they are soluble in strong acids, but I suppose that it is because they simply decompose in these conditions). MALDI-TOF is hard to apply here for the same reason: for totally insoluble polymers it is challenging to prepare homogeneous mixtures of the matrix and the anolyte (Wu and Odom, Anal. Chem. 1998, 70, 456A–461A). Other methods, such as NMR spectroscopy or FTIR spectroscopy, hardly give any clue about the polymerization degree.

Furthermore, it is problematic not only to determine the polymerization degree, but to understand the structure of the terminal groups. This turned out to be important for theoretical modeling of the Raman spectra, because the calculated spectra strongly depend on the nature of the oligomer terminations. For this reason, we currently have only a qualitative interpretation of the changes observed in the operando Raman spectroscopy experiments.

7. Are the crystal structures of NiTIB and CuTIB known?

CuTIB that was synthesized in this work was basically amorphous, as evidenced by powder XRD; no other studies of CuTIB have been reported yet to the best of my knowledge. Regarding NiTIB, there are two types of structures in the literature derived from the same XRD pattern. The first type is a herringbone structure shown in Figure R1 (Chen et al., Angew. Chem. Int. Ed. 2019, 58, 14731-14739; Cheng et al., Adv. Electron. Mater. 2017, 3, 1700107). The second type is a stacked structure shown in Figure R2 (Cai et al., Adv. Sci. 2020, 7, 1903109). The fact that there are two different crystal structures fitting the XRD pattern indicates that this XRD pattern is not very informative, which is not surprising because all peaks are broad and there are only three intensive signals.

After the Thesis was submitted, together with Prof. Andriy Zhugayevych we continued to study the properties of NiTIB. It was shown that the herringbone structure (Figure R1) is energetically favorable, while the π-stacked polymorph transforms into a herringbone structure within picoseconds in molecular dynamics simulations at room temperature. Additionally, it was shown that sliding of the macromolecules along each other in the herringbone structure has a low activation barrier (up to 0.1 eV per monomer for the two-monomer cell), so the macromolecule positions are not fixed at room temperature. This is one of the factors leading to
the broadening of the XRD peaks. If needed, I would be happy to discuss these new results during the Q&A session at the Thesis defense.

Figure R1. Proposed herringbone structure of NiTIB (a) and simulated vs. experimental XRD patterns (b). Reproduced with permission from Chen et al., Angew. Chem. Int. Ed. 2019, 58, 14731-14739. Copyright 2020, Wiley-VCH.

Figure R2. Proposed stacked structure of NiTIB (a) and simulated vs. experimental XRD patterns (b). Reproduced from Cai et al., Adv. Sci. 2020, 7, 1903109 under CC BY license. Copyright 2020, the Authors.

8. What is the oxidation state in the NiTIB compound in your study? In the Literature review it is claimed that Ni is in the 1+ state? But in your system (when it is polymerized) it is 2+ or…? Could it be confirmed by any analytical method?

The formal oxidation state of nickel in the pristine NiTIB is +2, because the ligand is formally a dianion and there are no other counter-ions in the structure that balance the charge. However, the calculations recently performed by Prof. Andriy Zhugayevych show that the charge at Ni is from +0.5 to +0.7, which is due to strong π-backbonding from the ligands; in other words, the formal oxidation state apparently poorly reflects the real picture. Ni 2p area of the X-ray photoelectron spectrum of NiTIB is typical for Ni(II) (see Figure 38 in the Thesis). I thought about measuring EELS for NiTIB in the pristine and reduced states (to check if nickel is involved in the redox processes), but unfortunately there is almost no difference between the EELS spectra of Ni(0) and Ni(II) (Jeangros et al., J. Mater. Sci. 2013, 48, 2893-2907), so interpretation of these data would lead to ambiguities.
9. You compared FTIR spectra of crystalline NiTIB with amorphous CuTIB. What is about their Raman spectra? Would you observe a shift of M-N related bands in Raman spectra depending on the metal core? What was the reason behind using two different wavelengths (lasers) for characterizing NiTIB with Raman?

Raman spectrum of CuTIB was added to Figure 21 and briefly discussed in section 5.1, p. 66. Like in case with the FTIR, Raman spectra of NiTIB and CuTIB had similar features, indicating that they share the same structural pattern. Vibrational spectra (both FTIR and Raman) typically weakly depend on the presence/absence of long-range ordering because they are affected mainly by the local environments (nm scale). The M-N related bands in CuTIB are shifted to lower frequencies, which is expected because Cu atoms are heavier than Ni. Measurements with different wavelengths are unnecessary for determining the vibrational frequencies; they were initially added to Figure 21 because there are operando Raman spectroscopy data for λ = 532 nm and 780 nm. The spectra for λ = 780 nm were removed from the revised Figure 21; these data can be found in Appendix A, Figure A8.

10. Coulombic efficiencies should be added to the graphs with prolonged cycling of materials in different cells (i.e. Figure 31, etc.)

Coulombic efficiencies were added to the revised Figure 33 and Figure 28.

11. If the redox processes are localized on the organic part of the polymer, would TIB display electrochemical activity with another non-metallic linker in a related polymeric compound (in case of anode materials)?

Although there are no experimental data for the free ligand, I suppose that it must be redox-active without the metal linkers. The oxygen-containing analog of TIB, dihydroxybenzoquinone, was reported as a battery cathode material (Hanyu et al., J. Power Sources 2013, 221, 186-190). Related polymeric compounds that contain structural fragments of TIB also show redox activity (Sun et al., CCS Chem. 2019, 1, 365-372; Wu et al., Angew. Chem. Int. Ed. 2015, 54, 7354-7358). However, the electrochemical properties of these polymers (i.e., charge-discharge profiles, redox potentials) are strikingly different from NiTIB. Although nickel is not reduced upon lithiation/sodiation/potassiation, it strongly affects the electronic structure of the material.

12. The manuscript contains some grammar and technical misprints:
   a. P 41: the limited specific surface area, the intercalation mechanism.
   b. P 42: the article should be added: in the 2+ state.
   c. P 90 (“Error. Reference source not found”)

The errors were corrected in the revised version of the Thesis.

**Response to Prof. Oleg Levin**

1. Experimental section. Why the component:carbon:binder ratio was different in different sets of experiment (anode applications, cathode applications, Ni or Cu complex). Can such inconsistence influence the quality of the obtained results?

During my PhD studies, all initial electrochemical tests (for both materials and for both cathode and anode applications) were performed with thin electrodes containing 50% wt. of carbon. Starting with high contents of carbon is a common practice for organic-based materials (see, for example, Peng et al., Nat. Energy 2017, 2, 17074; Dong et al., Nat. Energy 2020, 5, 1043-1050; Patil et al., Adv. Mater. 2017, 29, 1703373; Tang et al., J. Mater. Chem. A 2019, 7, 486-492), and it helps estimate intrinsic limits of the materials in loose conditions. The initial round of tests showed that NiTIB had promising features as an anode material. At the same time, NiTIB had modest characteristics as a cathode material. Likewise, the moderate performance of CuTIB showed that it would be uncompetitive from the practical perspective. Considering these results, I decided to focus on NiTIB as the anode material, which included the first steps of electrode design (decreasing the carbon content, varying the areal capacity). No such work was done for CuTIB, as well as for NiTIB as the cathode material – it was assumed that if the materials show moderate characteristics in loose conditions, the performance should be even worse with lower carbon contents. Fortunately, decent performance was achieved for NiTIB-based anodes with low carbon contents (10-15 wt.%). At this point, the data for the diluted electrodes were redundant (because they are less strict and farther...
from the industrial standards) and were not included to the Thesis for this reason. In the revised version of the Thesis (section 5.3.1, p. 79), I added a note that the performance of NiTIB was evaluated in the diluted electrodes as well: I also provided a reference to our paper where these data can be found.

Overall, the data presented in the Thesis are sufficient to conclude that the performance of NiTIB in the anodes is superior compared to CuTIB and to both materials in the cathodes. I agree that in some cases using various “component-carbon-binder” ratios can make it challenging to compare the electrochemical performance of electrode materials. For example, if one material has poor performance in the electrodes with a low carbon content, while the other one has promising features in the electrodes with a high carbon content, it is hard to draw conclusions even on the qualitative level. In the presented Thesis, however, qualitative conclusions can be made, considering the common knowledge that the characteristics of the materials (especially their specific capacities and high-rate capabilities) are typically better in thin electrodes with higher contents of carbon. It should also be stressed that the electrode compositions and areal loadings were nearly identical for CuTIB and NiTIB as cathode materials, as well as for NiTIB as the anode material for Li-, Na- and K-ion batteries.

2. Results and Discussion: Was the mass of the other cell components was considered while calculating the energy density for each active material?

Initially, the energy densities were calculated per mass unit of the active materials. In the revised version of the Thesis (section 5.2.1, pp. 73-75), I added estimation of the specific energies considering the masses of counter-ions required for the battery operation. It enables a more balanced comparison of the energy densities of CuTIB/NiTIB with other cathode materials. Although LiPF₆, which was consumed upon charging, originated solely from the electrolyte in my experiments, it is principally possible to use mixtures of solid salts and relatively small amounts of electrolyte (Yang et al., Nature 2019, 569, 245-250). For this reason, the total mass of the electrolyte was not considered.

Although for the end user of a battery the only meaningful value is energy density per total mass of the device, for the material scientists it is often convenient to use specific values per mass of the active materials. These values can be helpful for rough estimation of the total energy density of the batteries. They are typically calculated basing on the electrochemical output of half-cells, where alkali metals (added in large excess) serve as both reference and counter electrodes (Yang and Rogach, Adv. Energy Mater. 2019, 9, 1900747). Using this way of reporting the specific energy, as well as specific capacity and specific power of active materials is a common practice (Levin et al., Macromol. Chem. Phys. 2017, 218, 1700361; Fedotov et al., Nat. Commun. 2020, 11, 1484; Nguyen et al., Nature 2021, 593, 61-66).

3. Results and Discussion: Despite the extended discussion, the term “intercalation pseudocapacitance” do not have much sense in the scope of understanding the redox phenomena in the studied materials. For example, anodic CV curves on Fig. 32 exhibit sharp peaks, which, according to classification of Dunn et al (p. 29), are typical for “battery materials” with fast rate of charge compensating ion transfer in the lattice. At the same time cathodic CVs of the same materials are almost rectangular, corresponding to “pseudocapacitive materials”. Author do not discuss this difference.

As discussed in the Thesis, the redox behavior of NiTIB strongly depends on the operational potential range. In the ranges of 0.5-2.0 V vs. M⁰/M, the material shows features with sharp profiles and significant peak-to-peak separations (O1/R1, see Figure 33) that are typical for “battery materials”, as well as broad peaks with small peak-to-peak separations (O2/R2 and O3/R3), where the current almost linearly depends on the potential scan rate, which are attributes for supercapacitance as defined by Dunn et al. This is discussed in the Thesis in section 5.3.1, pp. 85-86. Possible reasons for such behavior are discussed there as well. Regarding the cathode-related applications, it is challenging to determine if the redox features are capacitive/pseudocapacitive. Making conclusions solely from the CV profiles might be misleading, and the I-v analysis can hardly be applied here because of the fast capacity decay. This is mentioned in the Thesis, section 5.2.1, p. 75.

4. By ex situ XPS participation of Cu in redox processes was confirmed, while in Ni complex the process is only ligand-based. Why participation of Cu do not give the additional capacity and Ni polymer has higher performance?

Rationalizing the modest specific capacity of CuTIB is a subject of further studies. The factors that affect the capacity can generally be related to both kinetics and thermodynamics. Kinetic factors include slow diffusion of ions within the particles or through SEI layers. They likely play a less significant role in this case for several
reasons. Firstly, the particle size of the ball-milled CuTIB is small, therefore the diffusion paths of ions within CuTIB should be short. Secondly, it is unlikely that properties of the SEI layers are dramatically different for NiTIB and CuTIB with the same standard electrolyte (1M LiPF₆ in EC:DMC). Thirdly, the capacity of CuTIB is rather small even at a low current density (50 mA g⁻¹). Thermodynamic factors are related to the structure of CuTIB and its lithiated forms. For example, reduction of Cu(II) to Cu(I) might lead to decreased redox potentials for complete (i.e., two-electron) reduction of the ligands. From the XPS data it might be proposed that the ligands are redox active, but it is hard to say to which extent. Additionally, it is yet unclear if all Cu(I) is oxidized back to Cu(II) upon delithiation, or if the reduction of copper is partially irreversible.

5. P. 94. Why during in situ XRD experiments charge and discharge time is so different?

The operando XRD experiments were performed for the initial charge-discharge cycle, which is accompanied by SEI formation upon lithiation/sodiation/potassiation of the working electrodes. Reduction of the electrolyte components at the electrode surface should be the main origin of the irreversible capacity. Another possible reason is irreversible reduction of the electrode material itself, but this is not the case for NiTIB, as evidenced by operando XRD and operando Raman spectroscopy. This is mentioned in the Thesis, section 5.3.2, pp. 96-97.

The suitable strategies to mitigate the irreversible capacity loss include optimizing the electrolyte composition or the binder structure, creating artificial SEI layers, or modulating the material particle size and specific surface area (Li et al., Nano Energy 2020, 77, 105143; He et al., Energy Storage Mater. 2019, 23, 233-251). This is mentioned in the Thesis, section 5.3.2, p. 97. Solving this issue for NiTIB is a subject of future studies.

Response to Prof. Chao Luo

No corrections were requested by this Jury Member.

Response to Prof. Viktoria Nikitina

1) One of the conclusions is that Cu-based material has a disordered structure, while in the thesis text there is no information on the XRD analysis of this compound. It is rather strange to read for the first time about the structure of CuTIB in the Conclusions section.

Crystallinity of CuTIB is discussed in section 5.1, p. 67. In the revised version of the Thesis, the discussion was expanded, covering possible reasons of the poor crystallinity of CuTIB and suggested approaches for its improvement.

2) There seems to be a contradiction between the stated morphology of NiTIB in p. 71: "The NiTIB particles appeared as ~200 nm long and 20-40 nm wide filaments" and the ball-milling procedure performed later. If the material is already nanosized to 20-40 nm, why ball milling was necessary?

Initially, the idea was to compare NiTIB and CuTIB that were synthesized and treated the same way, so the ball-milling was carried out for both materials. I agree that the ball-milling played an important role only for CuTIB where the particles were relatively large; for NiTIB, such treatment turned out to be less important for improving the electrochemical performance. For this reason, ball-milling of NiTIB was applied only for the first set of experiments (cathode-related applications, diluted thin electrodes). In later experiments (anode-related applications), no ball-milling was applied for NiTIB, which is indicated in the Experimental section and in section 5.3.1, p. 78.

3) It is not clear why the ratio NiTIB/carbon/binder was 4:5:1 when it is used as a cathode material and becomes 70:15:15 or 80:10:10 when it is tested as an anode material. Is there any logical explanation for such compositional differences?

During my PhD studies, all initial electrochemical tests (for both materials and for both cathode and anode applications) were performed with thin electrodes containing 50% wt. of carbon. Starting with high contents of carbon is a common practice for organic-based materials (see, for example, Peng et al., Nat. Energy 2017, 2, 17074; Dong et al., Nat. Energy 2020, 5, 1043-1050; Patil et al., Adv. Mater. 2017, 29, 1703373; Tang et al., J. Mater. Chem. A 2019, 7, 486-492), and it helps estimate intrinsic limits of the materials in loose
The initial round of tests showed that NiTIB had promising features as an anode material. At the same time, NiTIB had modest characteristics as a cathode material. Likewise, the moderate performance of CuTIB showed that it would be uncompetitive from the practical perspective. Considering these results, I decided to focus on NiTIB as the anode material, which included the first steps of electrode design (decreasing the carbon content, varying the areal capacity). No such work was done for CuTIB, as well as for NiTIB as the cathode material – it was assumed that if the materials show moderate characteristics in loose conditions, the performance should be even worse with lower carbon contents.

Fortunately, decent performance was achieved for NiTIB-based anodes with low carbon contents (10-15 wt.%). At this point, the data for the diluted electrodes were redundant (because they are less strict and farther from the industrial standards) and were not included to the Thesis for this reason. In the revised version of the Thesis (section 5.3.1, p. 79), I added a note that the performance of NiTIB was evaluated in the diluted electrodes as well; I also provided a reference to our paper where these data can be found.

4) In p. 79 it is stated that rate capability for NiTIB is higher in the ether-based electrolyte, which is because of its lower viscosity and higher ionic conductivity. Yet, the capacity is higher in ether-based electrolyte even at low charge-discharge rates, and there is no explanation for that. Besides, for thin electrodes the porosity effects should not be significant at 20C, and therefore electrolyte viscosity should not be important. Please comment.

The passage about possible reasons for better high-rate capabilities with the ether-based electrolyte was revised considering your comment (see section 5.3.1, p. 78). I suppose that one of the reasons could be the difference in the conductivities of the SEI layers that form during the initial cycles. This hypothesis can be probed using electrochemical impedance spectroscopy, which is a subject of future studies.

5) In p. 82 the author states that his material has a record areal capacity. Please explain why it is important for application in metal-ion batteries. Also please provide comparison between the volumetric energy densities (in Wh/L) for NiTIB used as an anode and LTO.

Besides the electrodes (active materials, conductive fillers, and binders), batteries contain separators, current collectors, sealing cases and other electrochemically inactive components. Making the electrodes thicker helps to increase the mass fraction of active components in the battery, thus improving the overall energy density of the device (Patry et al., Energy Sci. Eng. 2015, 3, 71-82). Additionally, it helps to decrease the battery cost per kWh and therefore make the production economically viable (Wood et al., J. Power Sources 2015, 275, 234-242). In modern Li-ion batteries, the areal capacities are typically ~3-4 mA h cm⁻² (Lin et al., Nat. Commun. 2018, 9, 5262). Brief discussion of this topic was added to the revised version of the Thesis, section 5.3.1, pp. 81-82.

I also added information about the densities of CuTIB and NiTIB to section 5.1, p. 64, and added discussion of the volumetric capacities of NiTIB and LTO to section 5.3.1, p. 87. The density of NiTIB is 1.5-1.6 times smaller than for LTO, while its specific capacity is ~1.5 times larger, so the volumetric capacities should be roughly the same.

Response to Prof. Shiyu Zhang

No corrections were requested by this Jury Member.