Accessing copper oxidation states of dissolved negative electrode current collectors in lithium ion batteries

A novel capillary electrophoresis (CE) method with ultraviolet–visible spectroscopy (UV–Vis) detection for the investigation of dissolved Cu$^+$ and Cu$^{2+}$ in lithium ion battery (LIB) electrolytes was developed. This method is of relevance, as the current collector at the anode of LIBs may dissolve under certain operation conditions. In order to preserve the actual oxidation states of dissolved copper in the electrolytes and to prevent any precipitation during sample preparation and CE measurements, neocuproine (NC) and ethylenediamine tetraacetic (EDTA) were effectively applied as complexing agents for both ionic copper species. However, precipitation and loss of the Cu$^+$-NC-complex for quantification occurred in presence of the commonly applied conducting salt lithium hexafluorophosphate (LiPF$_6$). Therefore, acetonitrile (ACN) was added to the sample in order to suppress this precipitation. Dissolution experiments with copper-based negative electrode current collectors in a LIB electrolyte were conducted at 60°C under non-oxidizing atmosphere. First findings regarding the copper species via CE revealed dissolved Cu$^+$ and mainly Cu$^{2+}$. However, primarily Cu$^+$ dissolved from the passivating oxide layer (Cu$_2$O and CuO) of the current collector due to the formation of acidic electrolyte decomposition products. Due to the instability of Cu$^+$ in the electrolyte a further disproportionation reaction to Cu$^0$ and Cu$^{2+}$ occurred. The results show the high potential of this CE method for prospective investigations regarding the current collector stability in new battery electrode formulations and correlations of dissolution events with dissolution mechanisms and battery cell operation conditions.

Keywords:
Capillary electrophoresis / Copper speciation / Current collector / Lithium ion battery / Transition metal dissolution

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

1 Introduction

LIBs are a key technology for portable electronic devices and electro mobility due to particularly superior high energy densities per volume at low costs [1–5]. For the operability of LIBs, transition metals (TMs) play a fundamental role as reversible lithium insertion hosts for positive electrodes in form of layered lithium metal oxides (LMO$_2$, $M$ = Ni, Co, Mn, {Al}), spinel type LiMn$_2$O$_4$ (LMO), or olivine type LiFePO$_4$ (LFP) materials [6–10]. TM dissolution from these materials and redeposition on the electrodes can accelerate electrolyte side reactions leading to a loss of active lithium and thus to a lower battery lifetime [11–22]. Also Al dissolution from the Al current collector at the positive electrode (cathode) can take place [23–26].

The current collector for the negative electrode (anode) is based on copper [27,28]. In contrast to positive electrode materials and aluminum, copper dissolution from negative current collectors and consequential negative effects on the cell performance were less investigated:

First findings by Aurbach and Cohen demonstrated an incomplete inertness of the copper foil due to remaining electrolyte contaminants [27]. Furthermore, electrochemical
The effective capillary length was 41.5 cm. Capillaries were obtained from Polymicro Technologies (Phoenix, AZ, USA). Electrochemically dissolved copper in presence of electrolyte is the proposed main species [29–32]. Moreover, the amount of electrochemically dissolved copper in presence of electrolyte impurities like H$_2$O or HF increased significantly [29]. In case of regularly charged-discharged LMO-based cells, Yang et al. identified deposited Cu$_2$O, MnO and MnO$_2$ on the negative electrode surface via scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) [33]. These deposits possibly lead to capacity loss by blocking the reversible lithium intercalation pathways into the material. The electrolyte additive 1,2,3-benzotrazole working as copper ion-scavenger significantly improved the cell performance [33]. The copper dissolution was mainly associated with copper corrosion by HF formed during the decomposition of the conducting salt LiPF$_6$ [33]. Dissolution experiments with copper foil in LIB electrolytes at elevated temperatures confirmed a correlation between HF formation and copper dissolution [33]. For a deeper understanding of the copper dissolution mechanism(s) from the negative electrode current collector and the impact on cell performance, investigations regarding dissolved copper species as well as quantitative information are indispensable. However, no attempts have been made on this topic so far to, e.g., prove the proposed dissolution of Cu$^+$ and the resulting impact on cell performance. Since the XPS technique primary enables the determination of the oxidation states of deposited TM species, e.g., on electrodes, a complementary new CE method with a higher sensitivity was developed to access the oxidation states of dissolved copper in organic carbonate-based electrolytes. As demonstrated in previous studies, CE has a high capability for the analysis of dissolved TM species and has already been applied for the investigation of Mn$^{2+}$ and Mn$^{3+}$ in LIB electrolytes [34–36]. However, investigations regarding Cu$^+$ or Cu$^{2+}$ speciation via CE have been not implemented so far. Our newly developed CE method was applied for the copper species analysis in electrolyte samples after dissolution experiments with copper current collectors under non-oxidizing atmosphere.

2 Materials and methods

2.1 Capillary electrophoresis conditions

Copper speciation was conducted with a 7100 CE System (Agilent Technologies, Santa Clara, CA, USA) with UV–Vis detection (Long-life Deuterium Lamps (8-pin) RFID tag, Santa Clara, CA, USA). The applied fused silica capillaries with 75 μm inner diameter, 365 μm outer diameter and 50 cm length were obtained from Polymicro Technologies (Phoenix, AZ, USA). The effective capillary length was 41.5 cm. Capillaries were preconditioned by rinsing 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). Subsequently, capillaries were flushed 2000 s with running buffer for equilibration. Before and after each run, capillaries were reconditioned for 300 s and 60 s with running buffer, respectively. The separation conditions were +30 kV with a voltage ramp of 30 s at a constant temperature at 25°C. Samples were injected hydrodynamically with a pressure of 50 mbar for 7 s, followed by the injection of running buffer under same conditions. Detection was performed simultaneously for Cu$^+$ at 225 nm, for Cu$^{2+}$ at 195 nm, and for the presented copper speciation at 270 nm.

2.2 Preparation of running buffer and standards

The applied running buffer (pH 9.2) comprised 25 mM sodium tetraborate (Na$_2$B$_4$O$_7$, for analysis, Merck) and 0.2 mM neocuprine (NC, ≥99.5%, Merck).

An ICP-standard (1000 mg/L, TraceCert®, Sigma–Aldrich, Buchs, Switzerland) was used for Cu$^{2+}$. For the Cu$^+$-standard (1000 mg/L), copper(I) chloride (for analysis, Emsure®, Merck) was dissolved under argon atmosphere in acetonitrile (ACN, HiPerSolv CHROMANORM®, VWR Chemicals, Fontenay-sous-Bois, France) containing NC at fivefold molar excess to Cu$^+$. Afterward, Milli-Q water was added to the solution (1:1, v/v) to obtain the desired concentration. The species independent quantification of copper was determined with inductively coupled plasma-optical emission spectrometry (ICP-OES) using an ARCOS (Spectro Analytical Instruments GmbH, Kleve, Germany) with an axial positioned plasma torch. The parameters and preparations were applied according to Vortmann and Evertz et al. [19, 37]. Contamination with Cu$^{2+}$ was regularly checked via CE. The Cu$^+$-standard was stored at 5°C under exclusion of light.

2.3 Determination of the recovery rate

The recovery rate was determined with saturated solutions of Cu$^+$ and Cu$^{2+}$ in a commonly used LIB electrolyte solution. In a glovebox, copper(I) chloride and copper(II) nitrate (97%, Sigma–Aldrich, Steinheim, Germany) were dissolved in electrolyte (1 M LiPF$_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) = 50:50 wt%, Selectilyte™ LP50, BASF, Independence, OH, USA). The remaining salts were removed by centrifugation at 8,500 rpm for 10 min (Galaxy 5D, VWR, Radnor, PA, USA). Total copper concentrations of the obtained solutions were determined with ICP-OES. Speciation and quantification in electrolytes were conducted via CE–UV–Vis with external calibration.

The water content in the used electrolyte was less than 30 ppm according to coulometric Karl-Fischer titration. The 851 Titrand Karl Fischer Coulometer (Metrohm, Herisau, Switzerland) was calibrated with a threefold measurement of a 100 mg/L water standard for quantification. Electrolytes...
were measured three times with an injection of 1 g, respectively. Instrument control, data acquisition and data evaluation were performed by tiamo™ 2.4 (Metrohm) [38].

2.4 Storage experiments

In advance, copper current collectors (Evonik Industries AG, Germany) were cleaned with Milli-Q water and cut subsequently into small slices (Ø ~ 5 mm). Copper slices were dried at 60°C in a vacuum drying chamber (Binder, Tuttlingen, Germany) for 2 days. Under argon atmosphere, 100 mg copper foil was immersed into 2 mL electrolyte (1 M LiPF6 EC/EMC = 50:50 wt%, BASF). The prepared samples were stored in self-made polyetheretherketone (PEEK) crimp top headspace vials (10 mL). Vials and crimp caps (Cap BI, hole 8 mm, 20 mm Si/PtFE, 45° shore A, 3 mm, VWR) were dried at 60°C for 2 days prior experiments. The vials were sealed with the crimp caps and silicone rubber (Adhesive Sealant, Momentive Performance Materials, Leverkusen, Germany). The samples were stored in a climate chamber (Binder) at 60°C for 21 days. Any precipitants in the electrolyte were removed after the storage experiments by centrifugation (8.500 rpm, 10 min, Galaxy 5D, VWR).

2.5 Sample preparation

Non-electrolyte containing copper samples were prepared via dilution with a NC-solution (100 mM, in ACN), followed by the addition of an EDTA solution (0.1 M, disodium salt in aqueous solution, Tritinorm, VWR Chemicals, Leuven, Belgium). Afterward, ACN and running buffer were added to achieve an ACN concentration of 37.5 vol% for optimal solubility of the Cu⁺-NC-complex. The concentrations of NC and EDTA in the prepared sample were 12.5 mM, respectively.

Recovering of the electrolyte samples was conducted in a glovebox. The sample preparation with aqueous buffers was performed under inert atmosphere using argon counterflow to prevent oxidation of Cu⁺ (Supporting Information).

3 Results and discussion

3.1 Species stabilization

The stabilization of both dissolved copper species was conducted with complexing agents in order to enable the investigation of both species via CE. Therefore, Cu⁺ was complexed with Cu⁺-selective NC to prevent the oxidation in contact with air, the favored disproportionation reaction to Cu²⁺ and Cu²⁺ and the precipitation of Cu₂O at neutral or alkaline pH [33,39–45]. Furthermore, the sample preparation was performed under a counter flow of argon to avoid oxidation of non-stabilized Cu⁺ by ambient O₂ (Supporting Information).

The observed precipitation of Cu²⁺ in the applied sodium borate-based running buffer at pH 9.2 was successfully prevented with EDTA, which also stabilized Cu⁺ regarding its reduction in presence of NC and reducing agents [39,46]. In a next step, the sample preparation order was optimized to avoid insufficient complexation and loss of Cu⁺ due to EDTA [39]. As demonstrated for iron speciation, spontaneous oxidation of insufficient complexed Fe²⁺ occurs in presence of EDTA and O₂ due to the formation of the Fe³⁺-EDTA-complex [34]. Since the sample preparation was performed under inert gas to prevent oxidation, loss of insufficient stabilized Cu⁺ can probably occur due to the favored disproportionation reaction. This was confirmed with a deaerated solution of dissolved CuCl in 2 vol% NH₃ under inert gas. The addition of EDTA to the solution led to a spontaneous precipitation of fine metallic copper particles due to an accelerated disproportionation reaction, impelled by the formation of the more stable Cu²⁺-EDTA-complex. Previous complexation of Cu⁺ with NC to an orange colored [Cu(NC)₂⁺]-complex successfully prevented the loss of Cu⁺. Therefore, a NC/ACN solution (100 mM NC) was applied since the coordination of ACN to Cu⁺ provides additionally stability of this species during sample preparation [42–45]. However, the formation of the more stable Cu⁺-NC complex was not interfered by ACN. For sufficient stabilization of Cu⁺, a final NC-concentration of 12.5 mM in the prepared sample was necessary to prevent partly formation of Cu²⁺. In order to verify optimal stability conditions for Cu²⁺ during sample preparation, a Cu²⁺-standard solution (0.39 mM) at neutral pH was investigated via CE–UV–Vis. This resulted in a negligible Cu⁺-concentration below LOD (LOD = 18.4 μg/L). Both complexed copper species were stable and loss of species were not observed during daily measurements.

3.2 Method development

To enable the separation of both oppositely charged copper complexes in one run, an alkaline borate-based running buffer was applied. The running buffer only contained additional 0.2 mM NC to stabilize the Cu⁺-NC-complex during CE measurements. The use of EDTA in the running buffer led to the precipitation of NC. Therefore, NC was no longer present to fully stabilize the Cu⁺-NC-complex during the measurements as shown by an increased baseline between the Cu⁺ and NC signal (Fig. 1A, black line). In contrast, no precipitation of NC was observed in an EDTA-free running buffer (Fig. 1A, red line). The pre-capillary complexation of Cu⁺ was sufficient and the Cu²⁺-EDTA-complex showed no decomposition during CE measurements (Fig. 1B). With optimized CE-parameters, the separation of Cu⁺ and Cu²⁺ was performed in ~4 min.

For optimal signals intensities, the peak heights for Cu⁺ and Cu²⁺ were determined with the developed method at defined wavelength between 195 and 340 nm in 5 nm steps. The obtained values were plotted against the related wavelength and fitted for having an overview (Fig. 2A). The Cu⁺-NC-complex (black line) showed a comparably higher overall
signal intensity than the Cu²⁺-EDTA-complex (red line). Three signal maxima for the Cu⁺-NC-complex were detected at 205, 225, and 275 nm with highest intensity at 225 nm. In contrast, no distinct signal maxima were obtained for the Cu²⁺-EDTA-complex. However, the highest intensities for the Cu²⁺-EDTA-complex were observed at 195 and 265 nm. The simultaneously determined baseline noise was highest at 195 and 200 nm, but decreased steadily with increasing wavelength (Fig. 2B). Consequently, 225 nm was chosen for the detection of Cu⁺ and 265 nm for Cu²⁺ due to a comparably high signal intensity at low baseline noise. For the following presented electropherograms, both species were additionally recorded simultaneously at 270 nm.

Afterward, the proof of concept for a LIB-related matrix was performed with Cu⁺, Cu²⁺ (0.16 mM each), and 1 vol% of commonly used organic carbonate-based LIB electrolyte containing 1 M LiPF₆ as conducting salt [4,47–49]. The addition of battery electrolyte to the sample led to precipitation of a red and slightly soluble complex [Cu⁺(NC)₃]PF₆. The precipitation of the Cu⁺-complex was confirmed with CE measurements of the obtained supernatant solution after centrifugation, showing the loss of the Cu⁺-signal (Fig. 3A). Precipitation of the Cu⁺-NC-complex was already observed for large amounts of nitrate, perchlorate, and halides in aqueous solutions [39,41]. However, these precipitates were successfully redissolved by addition of organic solvents like 2-propanol or ethanol to the aqueous solution [39,46]. In this work, ACN was added to the solution to a final concentration of 37.5 vol% to enhance an optimal solubility of the Cu⁺-complex. The obtained electropherogram of the same
The reproducibility of the peak areas and the migration time was conducted with a Cu\(^{2+}\) and Cu\(^{3+}\)-standard after multiple injections (Table 1; 0.16 mM each, \(n = 6\)). The LOD and LOQ were determined in accordance with DIN 32 645 using a multi-level-calibration (\(N = 10, n = 3\)).

The recovery rates for Cu\(^{2+}\) and Cu\(^{3+}\) were determined with solutions of CuCl and Cu(NO\(_3\))\(_2\), in a LIB electrolyte. Saturated solutions of both copper species were prepared to receive suitable copper ion concentrations in the electrolytes. The determined recovery rate for Cu\(^{2+}\) was 103.9% in contrast to 42.4% for Cu\(^{3+}\) in respect to the obtained copper concentrations by ICP-OES. The conducted CE-measurements also revealed dissolved Cu\(^{2+}\) for the prepared Cu\(^{3+}\)-electrolyte solution with a share of 29.1%. This resulted in a recovery rate for copper of 71.5%. Since the sample preparation was performed under argon atmosphere, oxidation of Cu\(^{3+}\) by ambient molecular oxygen can be excluded. Therefore, the formation of Cu\(^{2+}\) can be attributed to the disproportionation reaction of non-stabilized Cu\(^{3+}\) in the electrolyte to Cu\(^{2+}\) and Cu\(^0\) [44]. In contrast to the spontaneous precipitation of copper particles in aqueous solutions in presence of EDTA, no precipitated copper was observed in the electrolyte. A possible explanation was a slower disproportionation reaction of Cu\(^{3+}\) in the electrolyte, leading to the formation of smaller colloidal copper particles. In comparison to ICP-OES, the formed Cu\(^0\) could not be investigated via this developed CE method. However, the amount of colloidal Cu\(^0\) should be equal to the amount of dissolved Cu\(^{2+}\) in case of a disproportionation reaction. Taking the formed 29.1% of Cu\(^{2+}\) into account, the total recovery rate for copper reached 100.6%.

### 3.3 Copper dissolution in LIB electrolytes

The acidic copper dissolution from negative current collectors was investigated using a commercially applied LIB electrolyte. Several studies demonstrated the decomposition of these electrolytes over time during charge–discharge cycling and particularly at elevated temperatures forming various acidic decomposition products like HF or difluorophosphoric acid [50–57]. To promote the formation of acidic electrolyte decomposition products and the subsequent copper dissolution, the copper foil and electrolyte containing samples were stored under inert atmosphere for 21 days at 60°C.

Both copper species could be detected in all three electrolytes recovered after storage at elevated temperatures (Fig. 4A). Cu\(^{2+}\) was the main dissolved copper species in the electrolytes within a range of 85.3% (first sample) to 92.5% (third sample). Furthermore, the total copper ion concentration in the electrolytes differed widely within the samples with the highest concentration for the first sample and the lowest concentration for third sample (Fig. 4B).

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**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 Cu\(^{2+}\) and Cu\(^{3+}\).

|                | Cu\(^{2+}\) | Cu\(^{3+}\) |
|----------------|------------|------------|
| Peak area variation (%) | 1.9        | 1.7        |
| Migration time variation (%) | 0.2        | 0.3        |
| Linear range [\(\mu g/L\)] | \(10^{-50} \times 10^3\) | \(10^{-50} \times 10^3\) |
| \(R^2\)       | 0.9998     | 0.9997     |
| LOD [\(\mu g/L\)] | 68.2       | 78.3       |
| LOQ [\(\mu g/L\)] | 238.3      | 286.7      |
Figure 4. Representative electropherogram for a copper current collector/electrolyte sample stored at 60°C (A, red line) and the determined Cu\(^+\) and Cu\(^{2+}\) concentrations in the electrolytes for all three samples (B).

The main copper dissolution can be associated with the formation of acidic electrolyte decomposition products at elevated temperatures [33]. The observed divergences in the overall copper ion concentration among the samples was probably caused by a different contact surface between the copper foil and the electrolyte, e.g., when copper slices stick together. Elemental copper is generally inert against acidic dissolution in absence of O\(_2\) or oxidizing acids due to a higher standard redox potential compared to hydrogen [58]. Hence, the copper dissolution can be attributed to the acidic dissolution of the passivating oxide layer (Cu\(_2\)O and CuO) on the copper surface [58]. However, the passivation layer is mainly composed of the more favored Cu\(_2\)O at ambient temperatures [59]. Moreover, Cu\(_2\)O is less inert against dissolution by HF than CuO [58]. Consequently, ongoing formation of acidic electrolyte decomposition products led to continuous dissolution of primary Cu\(^+\) (Fig. 5, bold letters). Hence, less stable Cu\(^+\) could be detected, despite the observed instability of Cu\(^+\) in LIB electrolytes and consequential favored disproportionation reaction. However, the rate of the disproportionation reaction is mainly restricted to the Cu\(^+\) concentration in the electrolyte according to a first-order reaction. Therefore, the sample with the highest copper ion concentration showed the lowest Cu\(^+\)/Cu\(^{2+}\) ratio (Cu\(^+\)/Cu\(^{2+}\) = 0.08), while the sample with the lowest copper ion concentration had the highest Cu\(^+\)/Cu\(^{2+}\) ratio (Cu\(^+\)/Cu\(^{2+}\) = 0.17). Although partly dissolution of Cu\(^+\) from the oxide layer as well as low diffusion of O\(_2\) into the headspace vial during the dissolution experiments cannot be excluded. Therefore, oxidative corrosion of elemental copper or oxidation of dissolved Cu\(^+\) by O\(_2\) could have taken place to a small extent (Fig. 5, italic letters). The oxidation of dissolved Cu\(^+\) by O\(_2\) probably leads to the formation of highly reactive superoxide (O\(_2^{-}\)) which can react in a subsequent step with a further Cu\(^+\) to peroxide (O\(_2\)\(^{2-}\)) [44, 45]. These species probably react via a nucleophilic attack with the organic carbonate in the electrolyte, e.g., in a ring-opening reaction in case of cyclic carbonates like EC [60, 61].

These first results regarding copper species in LIB electrolytes demonstrated that dissolved Cu\(^+\) is not stable in state-of-the-art LIB electrolyte solutions and undergo a disproportionation reaction to Cu\(^0\) and Cu\(^{2+}\). However, this reaction did not take place immediately. Therefore, Cu\(^+\) can migrate during charge–discharge steps into the bulk electrolyte and subsequently redeposit as Cu\(_2\)O on the electrodes or react in the electrolyte to Cu\(^0\) and Cu\(^{2+}\) [33]. In addition to the reported copper deposition on the electrodes that can block the reversible lithium intercalation, the formation of small...
sized copper particles within the bulk electrolyte could block the pores in the separator, reducing the lithium movement between the electrodes [33]. However, in case of excessive copper dissolution also an internal short circuit is conceivable. Hence, the investigation of these copper particles and the resulting negative effects should be investigated in future work.

4 Concluding remarks

A novel CE–UV–Vis method for the investigation of dissolved \( \text{Cu}^+ \) and \( \text{Cu}^{2+} \) in LIB electrolytes was developed in this work. For this purpose, NC and EDTA were applied as complexing agents to preserve the actual oxidation states of the dissolved copper ions in the electrolytes. The use of NC in the first sample preparation step stabilized \( \text{Cu}^+ \) successfully against oxidation in contact with air and the favored disproportionation reaction to \( \text{Cu}_2^0 \) and \( \text{Cu}^{2+} \). The complexation of \( \text{Cu}^{2+} \) with EDTA in the second step effectively prevented the precipitation of \( \text{Cu}^{2+} \) in the alkaline borate-based running buffer. In order to enable the quantification of both copper species via CE, ACN was added to the sample to avoid the precipitation of the Cu–NC-complex in presence of the commonly used conducting salt LiPF$_6$ in LIB electrolytes. The optimized sample preparation and separation parameters finally enabled the investigation of both dissolved copper species in LIB electrolytes in <4 min with good sensitivity in low microgram per liter range. Hence, this method provides the basis for following investigations regarding copper speciation and quantification in LIBs.

Investigations regarding dissolved copper species in LIB electrolytes were conducted in this work for the first time. Therefore, dissolution experiments with copper current collectors in a commonly applied LIB electrolyte were performed under inert atmosphere at 60°C. CE measurements of the recovered electrolytes revealed the dissolution of \( \text{Cu}^+ \) and mainly \( \text{Cu}^{2+} \). The copper dissolution can be associated with the formation of acidic electrolyte decomposition products, e.g., HF and subsequent dissolution of the passivating oxide layer (mainly Cu$_2$O) of the current collector [33,58,59]. Since Cu$_2$O tends to dissolve more easily in presence of HF in comparison to CuO, continuous dissolution of particularly \( \text{Cu}^+ \) and subsequent disproportionation of \( \text{Cu}^+ \) to \( \text{Cu}_2^0 \) and \( \text{Cu}^{2+} \) can be proposed for these conducted experiments [44, 58]. As a consequence, \( \text{Cu}^{2+} \) was detected as the main copper species in the electrolyte. In conclusion, this new CE method enables further insights on dissolved copper species in cycled LIBs, the related copper dissolution mechanism(s) and consequential negative effects on cell performance.

The authors would like to acknowledge the German Federal Ministry of Education and Research (BMBF) for funding the project “MEET Hi-EnD III” (03XP0258A).

The authors have declared no conflict of interest.

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