

Electrodeposition of indium from non-aqueous electrolytes

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Electronic Supplementary Information (ESI)

Experimental

Chemicals

Indium(III) oxide (99.9%) was purchased from Thermo Fisher (Merelbeke, Belgium). Hydrogen bis(trifluoromethanesulfonyl)imide (80 % aqueous solution, 99.9%) was purchased from IoLiTec (Heilbronn, Germany). 1,2-Dimethoxyethane (anhydrous, 99%, DME), poly(ethylene glycol) (average molar mass 400 g mol⁻¹, PEG400), lithium bis(trifluoromethanesulfonyl)imide and tetrabutylammonium tetrafluoroborate (99%) were purchased from Sigma–Aldrich (Diegem, Belgium). Indium(III) chloride (99.995 %). PEG400 was dried on molecular sieves (3A) prior to use.

Synthesis of indium(III) bis(trifluoromethanesulfonyl)imide, In(Tf₂N)₃

Indium(III) bis(trifluoromethanesulfonyl)imide (In(Tf₂N)₃) was prepared by mixing In₂O₃ (1.2 g, 4.3 mmol) and H(Tf₂N) (7.7g, 26 mmol) in 50 mL of demineralized water. The solution was stirred for 48 h at 90 °C. Subsequently, the solution was filtered to separate the filtrate from insoluble In₂O₃. Excess of water was removed from the filtrate by using a rotary evaporator at 55 °C. The product was further dried on a vacuum line for 72 h at 90 °C, yielding a white powder (3.2 g, 39%). Immediately after drying, the product was stored in an argon-filled glovebox (with H₂O and O₂ concentrations below 1 ppm). FTIR (ATR, $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$): 3341 (H₂O), 1629, 1323 (SO₂), 1120 (SO₂), 1193 (CF₃), 1036 (SNS), 797, 771, 744 (CF₃), 651 (SNS), 597, 570 (CF₃). CHN found (calculated for C₆H₆F₁₈InN₃O₁₅S₆): C 6.37 (6.70)%, H 1.54 (1.13)%, N 3.18 (3.95)%.

Preparation of the organic electrolytes

The preparation of the organic electrolytes was always performed in a glovebox. For the majority of electrolytes, 0.4 mol dm⁻³ of In(Tf₂N)₃ and 0.4 mol dm⁻³ of dried InCl₃ were mixed in 5 mL of either DME or PEG400 which was dried on molecular sieves (3Å) for three days prior to synthesis until the final water content was less than 500 ppm. The water content in PEG400 was monitored using an automated coulometric Karl Fischer titrator (Mettler-Toledo, mode C20s). InCl₃ was dried on a vacuum line for 72 hours at 90 °C prior to use. Dissolution of both indium salts in DME was observed to occur nearly instantly. In PEG400, it was necessary to rigorously stir overnight using a magnetic stirring bar at 500 RPM to achieve complete dissolution. Both electrolytes appeared to be colourless and were stored in closed vessels in a glovebox.

Electrochemistry

For all electrochemical experiments, an Autolab PGSTAT 302N electrochemical interface was used that was controlled by a computer with NOVA2 software. Cyclic voltammograms (CVs) and electrochemical depositions were conducted in an argon-filled glovebox. For the measurement of the electrochemical windows of the solvents, a platinum wire or a molybdenum wire embedded in glass, with a diameter of 1 mm was used as working electrode. For electrochemical depositions, platinum-coated silicon wafer pieces (silicon covered with 500 nm of silica, 10 nm of titanium and 100 nm of platinum) and molybdenum-coated soda lime glass substrates (500 nm) were used as working electrodes. The area of these working electrodes was approximately 20 mm². Prior to measurements, platinum wires and platinum-coated silicon wafer pieces were washed with HCl (35%), rinsed with

demineralized water and acetone, and dried. Molybdenum wires and molybdenum-coated soda lime glass substrates were washed with aqueous ammonia solution (6N), rinsed with demineralized water and acetone, and dried. Counter electrodes consisted of high-purity metallic indium plates (99.97%) or coiled platinum wires whose area was at least ten times larger than those of the working electrodes. These plates received cleaning steps analogous to those of the platinum-coated wafer pieces. A ferrocene/ferrocenium reference electrode was used that consisted of a glass tube filled with a solution of ferrocene (5 mmol L⁻¹) and ferrocenium (5 mmol L⁻¹) in the commercially available ionic liquid *N*-butyl,*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMP][Tf₂N], in which a platinum wire was immersed. Usage of this reference electrode enabled the possibility to mutually compare CVs of various indium-containing electrolytes. A ceramic crucible was used as electrochemical cell in which 3 mL of electrolyte was added. For measurements at elevated temperatures, the crucible was inserted into a copper heating block that was placed on an electric heating element. The temperature of the electrolyte was monitored using of a thermocouple that was enveloped in a chemically resistant glass sleeve. As mentioned before, electrochemical Quartz Crystal Microbalance (EQCM) measurements were done using platinum-covered QCM-crystals (1 inch, 5 MHz AT-cut platinum-coated crystals, INFICON) with an electrochemically active surface of 1.28 cm². Experiments were executed at room temperature, 100 °C and 160 °C, using a EQCM device (MaxTek) that was connected to an Autolab PGSTAT 302N electrochemical interface. Coiled platinum wires were used as counter electrode and the ferrocene/ferrocenium based electrode as reference electrode. For rotating ring disk measurements, a ring-disk electrode was used of which both the ring and the disk electrodes were made of gold (Pine instruments, AFE6R2AUAU). The diameter of the disk was 5.5 mm while the inner and outer diameter of the ring were 6.5 mm and 8.5 mm, respectively. The distance between the ring and disk was 1 mm and the theoretical collection efficiency of the ring equalled 38 %. Platinum plates were used as counter electrodes and the ferrocene/ferrocenium based electrode as reference electrode.

Characterization techniques

The morphology of the indium deposits on various substrates was studied using scanning electron microscopy (SEM; Phillips XL-30 FEG). Elemental analysis was done with energy-dispersive X-ray analysis (EDX; Octane elite super silicon drift detector, Ametek EDAX). Generated nanoparticles in electrolytes were imaged using transmission electron microscopy (TEM). TEM measurements were performed with a 80 kV Zeiss EM900, using 300 mesh Formvar/carbon-coated copper grid. Samples were prepared by diluting the electrolyte in acetone in a ratio of 1:4. The solution was sonicated for 30 min. Consequently 2 drops of the solution were placed on the TEM grid, which was allowed to dry overnight.

“Calculation cathodic current efficiency (CCE) EQCM data

The CCE of the deposition process was determined by comparing the charge generated in the cathodic wave of the CV with the charge calculated from the experimentally deposited mass. This mass is linearly proportional to the frequency change of the EQCM crystal, and can thus be calculated using the Sauerbrey equation:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\mu\rho}} \Delta m = -C_f \Delta m \quad (\text{Eq. s1})$$

where f_0 is the frequency of the crystal (Hz), μ is the shear modulus of quartz (2.947×10^{11} g cm⁻¹ s⁻²), ρ is the density of quartz (2.648 g cm⁻³), Δf is the frequency change (Hz), Δm is the mass change, and C_f is the sensitivity factor. C_f is required for the calculation of the deposited mass. This factor can be found by calibration of the crystal with a "model" electrolyte from which completely reversible deposition can be achieved. For the platinum crystal that was used in the experiment, the reciprocal of C_f equalled 2.2653×10^{-8} g Hz⁻¹ cm⁻². By using this factor, the highest amount of deposited mass was calculated, equalling roughly 400 μ g. When it is taken in consideration that the deposition process is in fact a three-electron process, in which the trivalent indium cation is reduced to metallic indium, the consumed charge can be found through Faraday's law of electrolysis:

$$m = \left(\frac{Q}{F}\right) \left(\frac{M}{z}\right) \quad (\text{Eq. s2})$$

where m is the mass (g), Q is the charge (C), F is the Faraday constant (96485 C mol⁻¹), z is the amount of electrons involved in the process and M the molar mass of the material (g mol⁻¹). By filling in all the factors and transforming the equation, the consumed charge of the deposition process was found, and by taking the ratio of this value with the charge obtained by integrating the cathodic current of the CV, a CCE of 114% was calculated. Naturally this is an overestimation, as the CCE cannot exceed 100 %. This discrepancy is due to the fact the cathodic current in the CV is not fully cathodic. The EQCM experiment indicated that during the measurement of the CV, in the range between -0.7 V vs. Fc^+/Fc and -0.4 V vs. Fc^+/Fc in the backward scan, stripping of indium to indium(I) already occurred. Hence, integration of this reduction wave will not give the charge that is only consumed during reduction, and will therefore lead to an error in the calculation of the CCE. The CV must be deconvoluted to extract the true cathodic part of the observed negative current, however, such analysis is not performed in this study.

Analogous calculations, using CV and QCM data obtained for the electrolyte composed of 0.4 mol dm⁻³ of $\text{In}(\text{Tf}_2\text{N})_3$ and 0.4 mol dm⁻³ of InCl_3 in PEG400, at 100 °C and 160 °C, were performed to determine the cathodic current efficiencies at both temperatures. At 100 °C, and 160 °C, the cathodic current efficiencies equalled 82 % and 0 %, respectively. "

Furthermore, a curve of mass/charge (M/z) as a function of the potential was constructed based on Faraday's law and the Sauerbrey equation:

$$\frac{M}{z} = -\frac{FC_f\Delta f}{\Delta Q} \quad (\text{Eq. s3})$$

where M (g mol⁻¹) is the molar mass of the species that is undergoing an electrochemical reaction, z is the number of electrons involved in the electrochemical reaction, $F = 96,485.34$ (C mol⁻¹) is the Faraday constant, and ΔQ (C cm⁻²) is the change in charge consumed during the electrochemical reaction. Eq. s3 can be used to determine M/z as a function of applied potential, which allows to examine changes in reaction mechanisms during the measurement of a CV. However, when the current in the CV goes through zero, experimentally determined M/z values become uncertain.

Therefore, these M/z values are removed from the graph. Negative values of charge changes ΔQ are used in eq. s3, so that M/z has an opposite sign as Δm , *i.e.*, negative for deposition and positive for a stripping process.

Fig. 1 shows the CV and EQCM data analyzed for M/z of an electrolyte composed of 0.4 mol dm^{-3} of $\text{In}(\text{Tf}_2\text{N})_3$ and 0.4 mol dm^{-3} of InCl_3 in DME. The value of M/z when indium(III) is reduced to indium(0), and thus being deposited with 100% efficiency, is $-38.27 \text{ g mol}^{-1}$. From Fig. s1, it was observed that experimental M/z values obtained during the onset of indium reduction, at approximately $-0.4 \text{ V vs. Fc}^+/\text{Fc}$, start at quite negative values. At this stage, indium(III) is mainly reduced to indium(I). Indium(I) is not reduced further to indium(0) and is lost in solution due to disproportionation. As the potential is shifted to more negative values, the reaction rate for the reduction of indium(I) to indium(0) is increased and the M/z values moved toward values more positive than $-38.27 \text{ g mol}^{-1}$, indicating that both reduction of indium(III) to indium(0) occurs, as well as reduction of indium(III) to indium(I), which subsequently undergoes disproportionation. From $-0.70 \text{ V vs. Fc}^+/\text{Fc}$ in the forward scan to $-1.1 \text{ V vs. Fc}^+/\text{Fc}$ in the backward scan, the curve remains nearly constant around the M/z value of $-38.27 \text{ g mol}^{-1}$, indicating that the predominant process is reduction from indium(III) to indium(0). From $-1.1 \text{ V vs. Fc}^+/\text{Fc}$ to $-0.72 \text{ V vs. Fc}^+/\text{Fc}$ in the backward scan, M/z values lower than $-38.27 \text{ g mol}^{-1}$ are obtained, and are once more attributed to the simultaneous occurrence of reduction of indium(III) to indium(0) and the reduction of indium(III) to indium(I), which undergoes disproportionation. After $-0.72 \text{ V vs. Fc}^+/\text{Fc}$ in the backward scan, the value strongly increases towards positive values, although the current in the CV is still negative. It was observed from the frequency response of the quartz-crystal that mass loss started to occur. Here, indium(0) is already being stripped to indium(I). However, simultaneously, reduction of indium(III) to indium(I) still occurs, resulting in a negative net current.

When the potential further shifts towards more positive potentials in the backward scan, M/z values become increasingly positive as the current in the CV goes through zero. The values remain high throughout the complete oxidation process and have been cut from the figure.

Figures

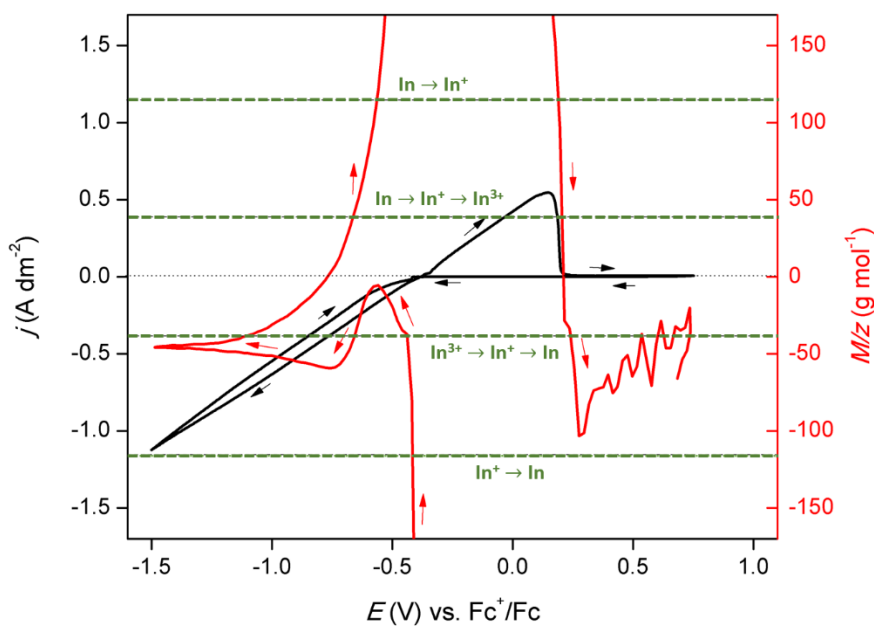


Figure s1: CV (2nd cycle) of an electrolyte composed of 0.4 mol dm^{-3} of $\text{In}(\text{Tf}_2\text{N})_3$ and 0.4 mol dm^{-3} of InCl_3 in DME on a platinum working electrode at room temperature (black line, left axis) with EQCM data analyzed for M/z (red line, right axis). Scans were recorded with a scan rate of 5 mV s^{-1} .

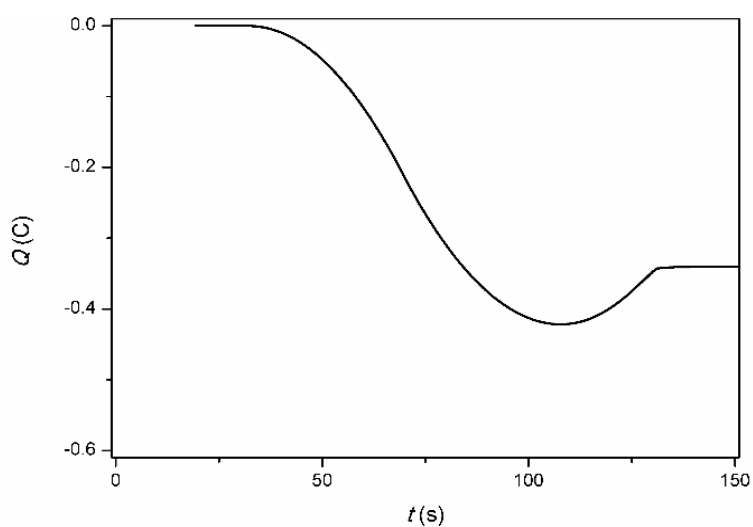


Figure s2: Q vs. t plot integrated for a CV for 0.4 mol dm^{-3} of $\text{In}(\text{Tf}_2\text{N})_3$ and 0.4 mol dm^{-3} of InCl_3 in DME on a platinum electrode, at room temperature with a scan rate of 0.5 mV s^{-1} .



Figure s3: Electrolyte composed of 0.4 mol dm^{-3} of $\text{In}(\text{Tf}_2\text{N})_3$ and 0.4 mol dm^{-3} of InCl_3 in DME, before (left) and after (right) the measurement of a CV at room temperature on an gold disk electrode with a scan rate of 5 mV s^{-1} .

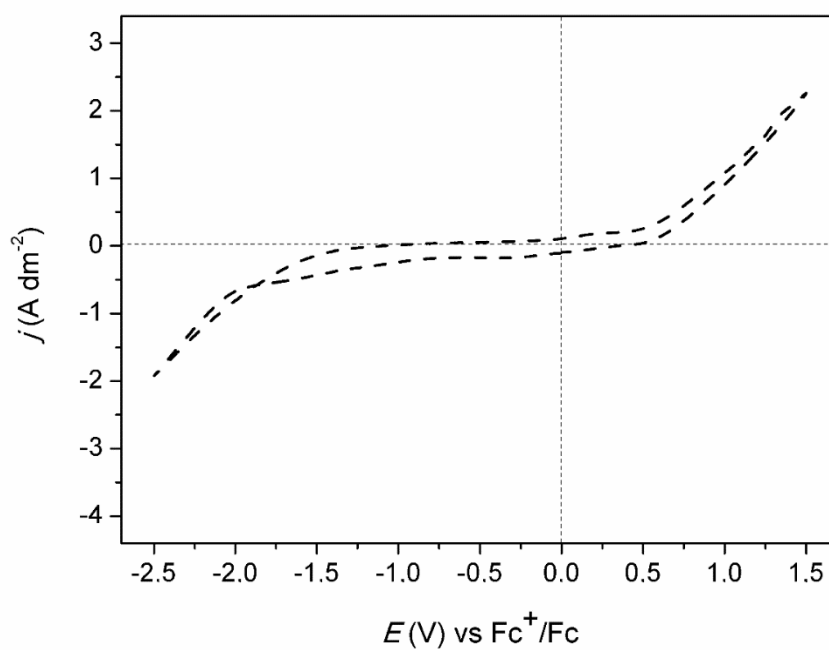


Figure s4: Electrochemical window of PEG400, with 0.1 mol dm^{-3} of $\text{Li}(\text{Tf}_2\text{N})$ as background electrolyte, measured on a platinum electrode at $160 \text{ }^\circ\text{C}$, with a scan rate of 50 mV s^{-1} .

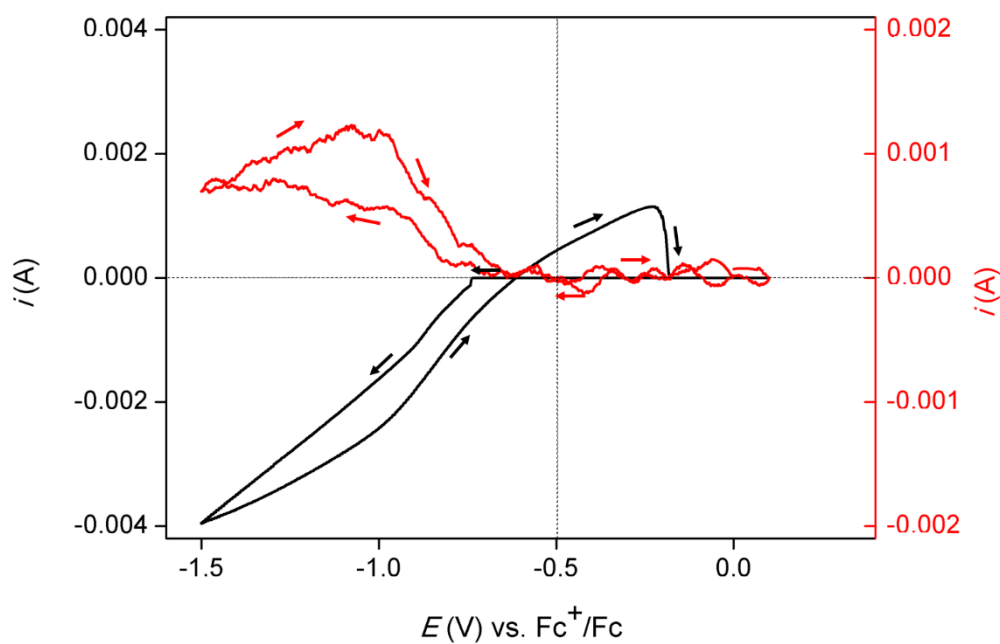


Figure s5. Disk and ring currents recorded in of 0.4 mol dm^{-3} of InCl_3 and 0.4 mol dm^{-3} of $\text{In}(\text{Tf}_2\text{N})_3$ in DME at 200 rpm at room temperature. The disk current was generated from the cyclic voltammetry with a scan rate of 5 mV s^{-1} , and the ring was kept at a potential of +1.0 V vs. Fc^+/Fc . The ring current data was smoothed by a Savitzky-Golay function with 40 points window size.