

Electrodeposition of indium from indium(III) methanesulfonate in DMSO

Wouter Monnens, Clio Deferm, Koen Binnemans and Jan Fransaer*

Electronic Supplementary Information (ESI)

Determination of the maximum experimental collection efficiency of the rotating ring disk electrode (RRDE)

The collection efficiency of the ring of the RRDE was determined using the ferrocyanide/ferricyanide reversible half reaction. The RRDE was immersed in a solution of 30 mmol dm⁻³ K₃Fe(CN)₆ in 1.0 mol dm⁻³ of KNO₃ and operated at rotation speeds between 400 and 2,000 rpm. A coiled platinum wire (diameter of 1 mm) and a platinum wire (diameter of 1 mm) served as counter electrode (CE) and reference electrode (RE), respectively. At each rotation speed, a CV was measured on the disk, in which a reduction current occurred that corresponded to the reduction of ferricyanide to ferrocyanide:



The ring was held at an overpotential of +0.80 V vs. Pt. Consequently, ferrocyanide formed at the disk was captured at the ring and oxidized back to ferricyanide:



The experimental results are presented in figure S3. Evidently, cathodic limiting currents ($I_{L \text{ disk}}$) recorded on the disk, and anodic limiting currents ($I_{L \text{ ring}}$) recorded on the ring increase with larger rotation speeds. The subsequent measured ratio of the limiting currents observed at the ring and disk is the empirical collection efficiency (N) and equals 35.1 % ± 0.8.

$$N = \left| \frac{I_{L \text{ ring}}}{I_{L \text{ disk}}} \frac{n_D}{n_R} \right| \quad (\text{S3})$$

where n_D and n_R are the number of electrons involved in the reaction at the disk and ring, respectively.

Construction of M/z vs. potential plot

To study the indium electrodeposition mechanism further, a curve of mass/charge (m/z) as a function of the potential was constructed based on Faraday's law and the Sauerbrey equation:

$$\frac{M}{z} = - \frac{F C \Delta f}{\Delta Q} \quad (\text{S4})$$

where M (g mol⁻¹) is the molar mass, z is the number of electrons involved in the electrochemical reaction, $F = 96485.34$ (C mol⁻¹) is the Faraday constant and ΔQ (C cm⁻²) is the change in charge consumed by the oxidation or reduction reaction. Equation (S4) can be used to determine M/z as a function of applied potential, which allows to identify the amount of involved electrons in the reduction and oxidation features. However, when the current in CV goes through zero, experimentally determined M/z values become uncertain. Therefore, these M/z values are removed from the graph. In this paper, we use the

absolute negative value of charge change ΔQ , so that M/z has an opposite sign as Δm , *i.e.* negative for deposition and positive for a stripping process. In figure S2, the resulting M/z vs. potential plot is shown. The onset in reduction current leads to a decrease in M/z until a value of around -38.27 is reached. This corresponds to a three electron reduction process, *i.e.*, reduction of indium(III) to indium(0). In the backward scan, the M/z value gradually decreases towards more negative values, indicating that the according process is not purely indium(III) to indium(0) anymore. Possibly, a fraction of indium(III) reduces to indium(I), which is not further reduced to indium(0). Formation of indium(I) during the observed reduction wave in the cyclic voltammogram is demonstrated in the performed RRDE experiment, discussed in the main text and presented in figures 4 and S4. As reduction of indium(III) to indium(I) is a two electron process, the M/z value is more negative than -38.27, equaling 57.41. When the reduction current passes through zero, the M/z value tends to decrease to even more negative values, after which it rapidly increases upon initiation of the oxidation current. The M/z value increases until a value of around 114 is reached, after which it remains relatively stable. The according process involves one electron, and is stripping of indium to indium(I).

Figures

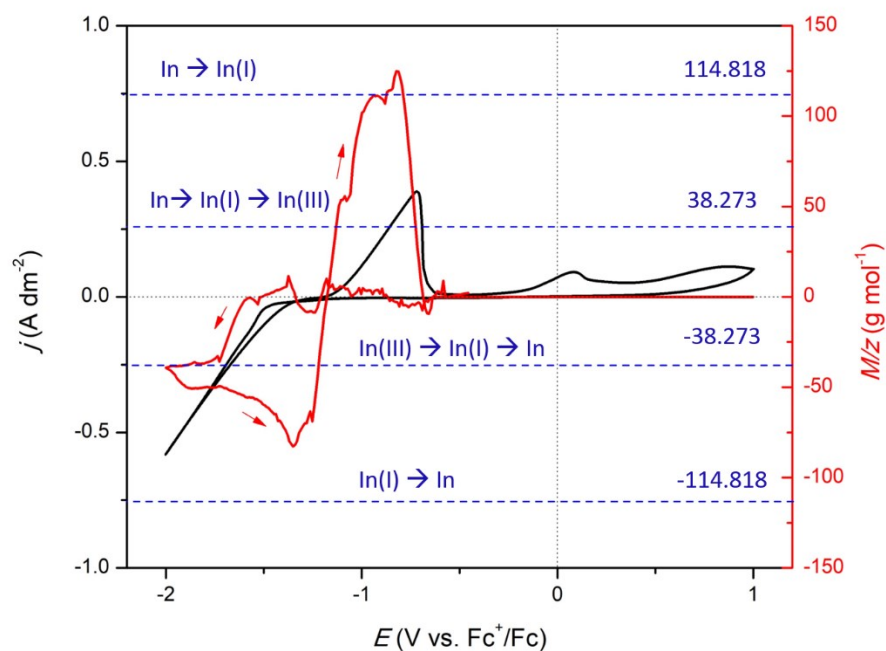


Figure S1: CV of $0.25 \text{ mol dm}^{-3} \text{ In}(\text{CH}_3\text{SO}_3)_3$ in DMSO on a platinum-coated QCM crystal at $26 \text{ }^\circ\text{C}$ (black line, left axis) with EQCM data analyzed for M/z (red line, right axis). Scans were recorded with a scan rate of 10 mV s^{-1} .

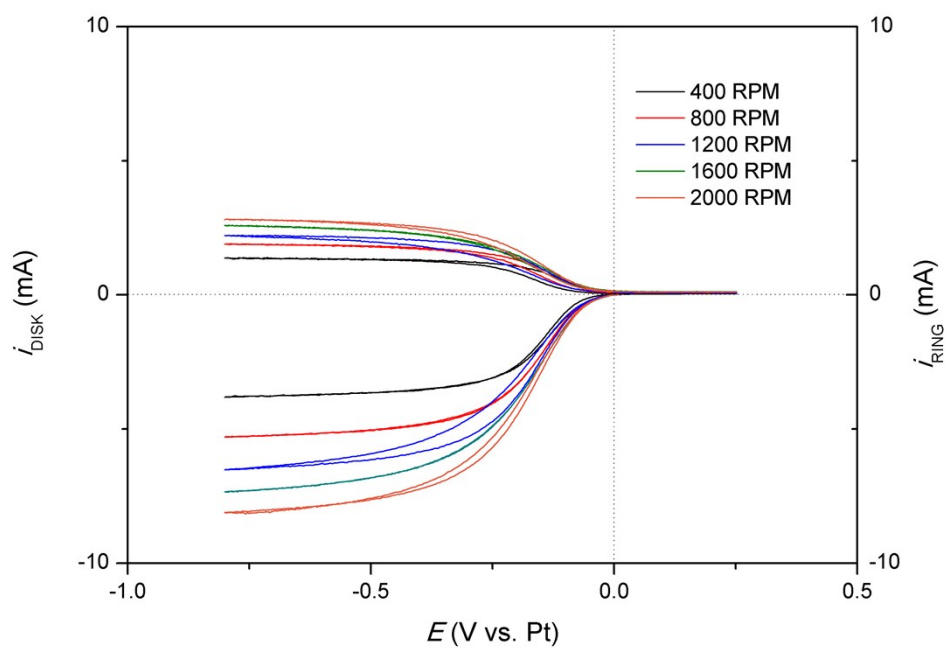


Figure S2: Disk (left axis) and ring (right axis) currents recorded in $0.03 \text{ mol dm}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6$ in $1.00 \text{ mol dm}^{-3} \text{ KNO}_3$ at various rotation speeds at room temperature. The disk current was generated from the cyclic voltammetry at a scan rate of 10 mV s^{-1} , and the ring was kept at a potential of $+0.8 \text{ V vs. Pt}$.

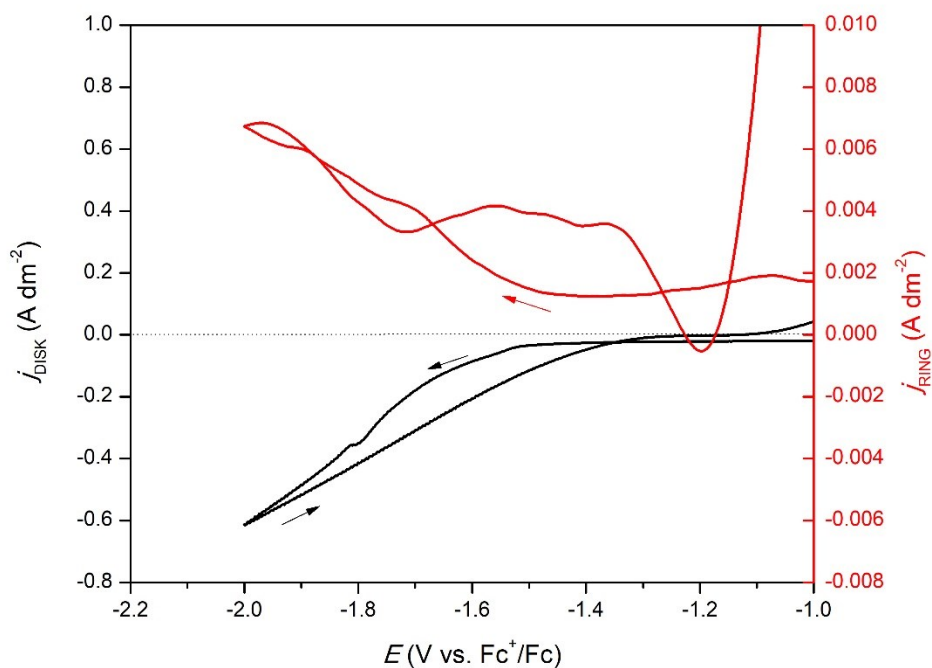


Figure S3: RRDE experiments. Disk (left axis) and ring (right axis) currents recorded in 0.25 mol dm^{-3} of $\text{In}(\text{CH}_3\text{SO}_3)_3$ in DMSO at 200 rpm at 26°C . The disk current was generated from the cyclic voltammetry with a scan rate of 10 mV s^{-1} , and the ring was kept at a potential of $+0.5 \text{ V vs. Fc}^+/\text{Fc}$.

Table S1: Diffusion Coefficient of indium(I), at 26°C .¹

T_s (s)	ω (RPM)	D ($\text{m}^2 \text{ s}^{-1}$)
4.1	50	3.4×10^{-10}
1.9	100	4.3×10^{-10}
1.0	200	3.7×10^{-10}
0.7	300	3.2×10^{-10}
0.5	400	3.7×10^{-10}
Average		$3.6 \pm 0.4 \times 10^{-10}$

1. Diffusion coefficients of indium(i) calculated using experimentally determined transit times at various rotation speeds, the kinematic viscosity ($7.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$) and a geometric proportionality constant, K (7.49).

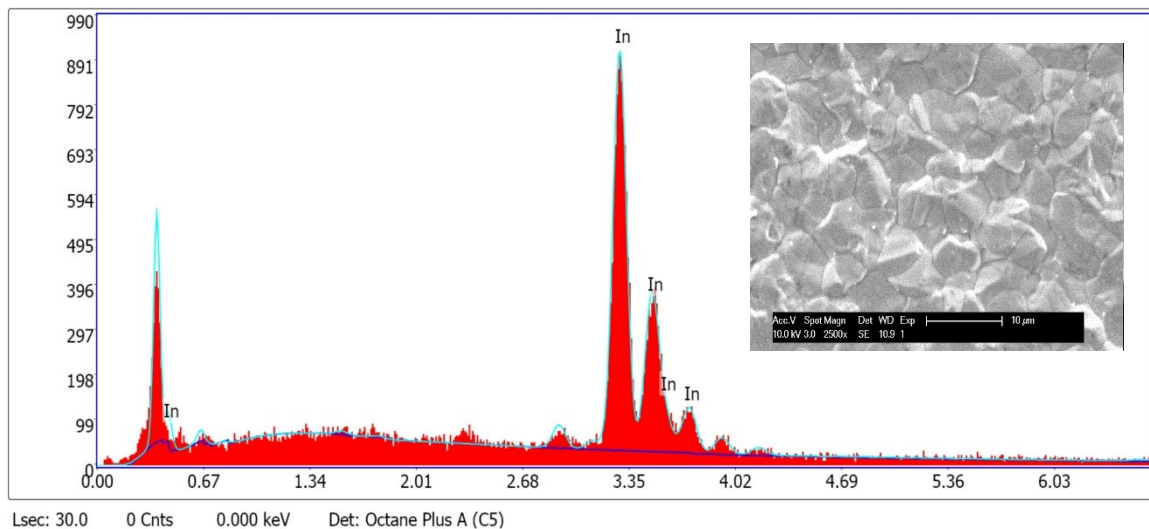


Figure S4: EDX spectrum and SEM image of indium electrodeposited on glassy carbon from at -2.0 V vs. Fc^+/Fc at 26 °C for 30 min from 0.25 mol dm^{-3} of $\text{In}(\text{CH}_3\text{SO}_3)_3$ in DMSO. The applied acceleration voltage was 10 keV.

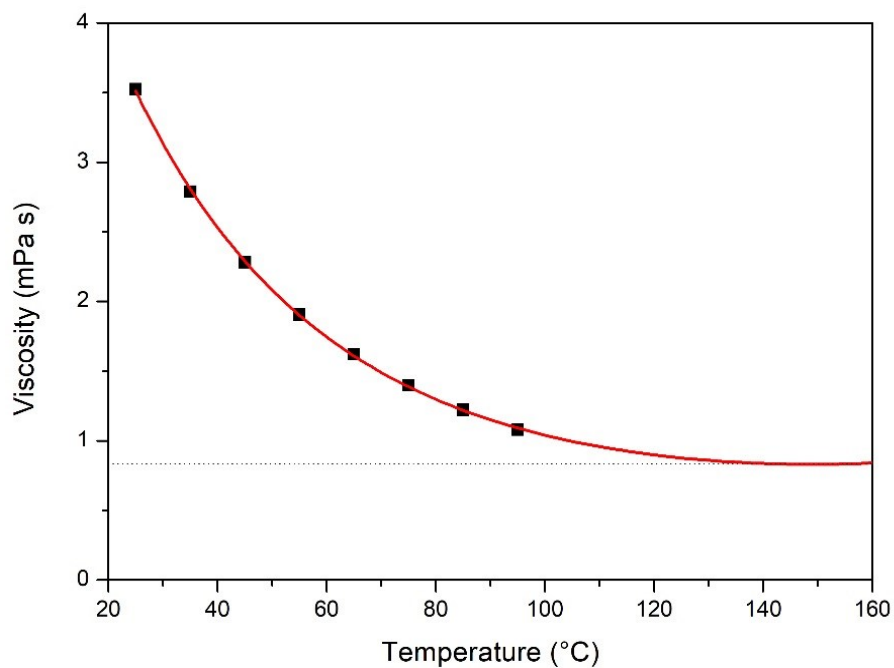


Figure S5: Viscosity as a function of temperature for 0.25 mol dm^{-3} of $\text{In}(\text{CH}_3\text{SO}_3)_3$ in DMSO. Viscosity values are extrapolated to 160 °C by exponential fitting.

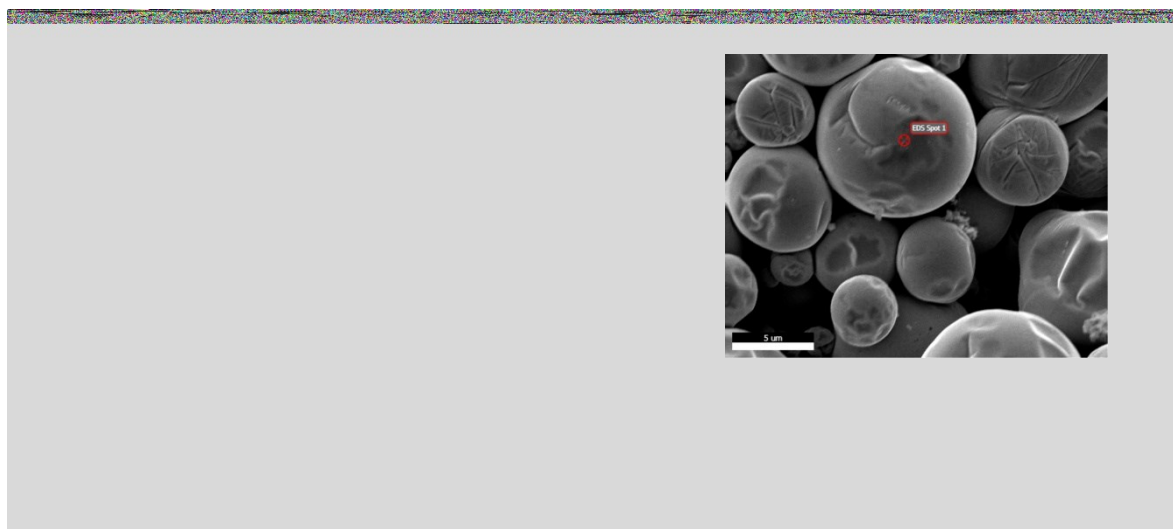


Figure S6: EDX spectrum and SEM image of indium electrodeposited on glassy carbon at -2.0 V vs. Fc^+/Fc at 160 °C for 30 min from 0.25 mol dm^{-3} of $In(CH_3SO_3)_3$ in DMSO. The applied acceleration voltage was 10 keV.

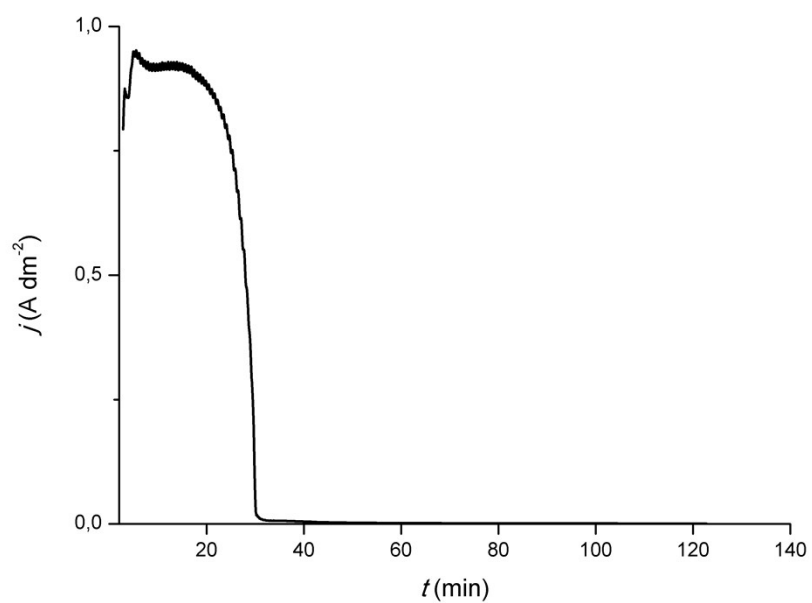


Figure S7: Stripping current, obtained by applying a potential of +0.1 V vs. Fc^+/Fc on an indium layer deposited at -2.0 V vs. Fc^+/Fc for 1 hour from 0.25 mol dm^{-3} of $\text{In}(\text{CH}_3\text{SO}_3)_3$ in DMSO.

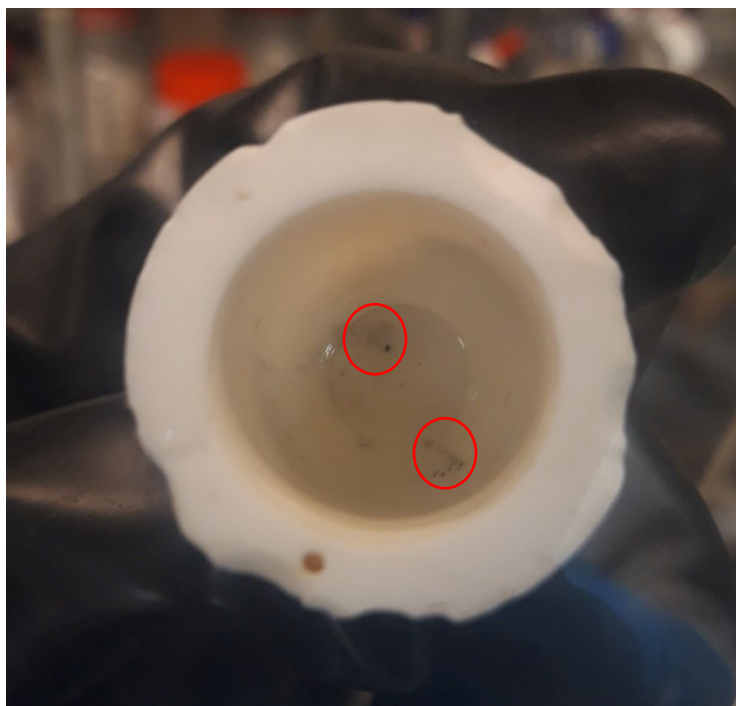


Figure S8: Picture of indium 'chunks' found in the solution after stripping deposited indium predeposited on a platinum substrate at +0.1 V vs. Fc^+/Fc at room temperature for one hour.

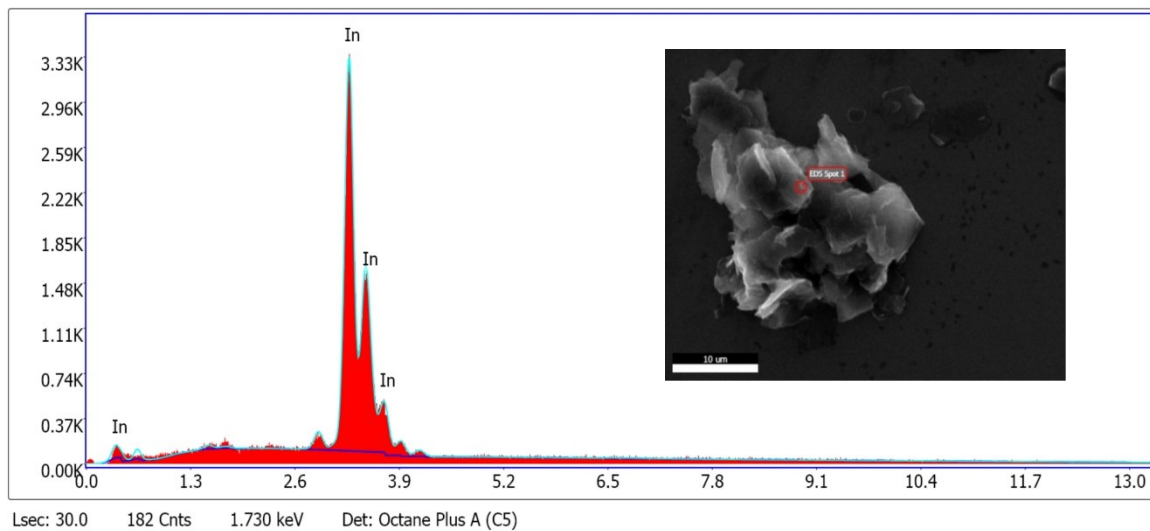


Figure S9: EDS spectrum and SEM image of isolated indium 'chunks' placed on a platinum substrate. The applied acceleration voltage of was 15 keV.