AN ELECTROCHEMICAL STUDY OF INDIUM BEHAVIOUR IN THE FUSED NaCl-KCl MIXTURE

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As the photoconductor applications of indium increase, more attention has been devoted to indium recovery. An electrochemical method may be suitable. The electrochemical properties of indium are rather poorly known; however, it seems that indium electrowinning may be done in a fused salt medium such as alkaline chloride mixtures.

We have studied the indium electrochemical properties in a NaCl-KCl mixture. No previous data exist in literature. However, some similarity can be expected with the indium salts electrochemistry in the fused LiCl-KCl equimolar melt, which has been investigated by Laitinen et al. (1) and other research groups (2-4). They obtained some evidence for mono- and trivalent indium ions.

We first tried to characterize the mono- and trivalent indium compounds in the fused equimolar NaCl-KCl mixture, and we measured the In/In(I) equilibrium potential. Afterwards, we studied the kinetics of the electrochemical reactions between indium species.

1. STABLE OXIDATION STATES OF INDIUM

1.1. Theoretical Considerations

Using the free energy of formation (5), we computed the standard potentials $e_\text{In/In(I)}^\circ$ and $e_\text{In/In(III)}^\circ$. These values and some physical properties of indium and its compounds are reported in Table 1.

| Compound | $T_\text{mp.}$(°C) | $T_\text{b.p.}$(°C) | $\Delta G^\circ_f$(J.mol.$^{-1}$) | $e_\text{x In/In(X)/Ag/Ag(I)}^\circ$ |
|----------|-----------------|-----------------|-----------------------------|----------------------------------|
| In       | 156             | 2000            |                             |                                  |
| InCl     | 225             | 608             | -140 330                    |                                 |
| InCl$_3$ | 586 Sub(300)    | ** - 335 000    | * 0.630 V ** -0.390 V       |

* values at 700°C  ** values estimated from data for gases and solids

Table 1 – Thermodynamic data and standard potentials.
From these data, it can be seen that mono- and trivalent indium salts could be stable in the fused NaCl-KCl equimolar mixture.

1.2. Experimental Results

The experimental apparatus that was used has been described previously (6). The solvent was contained in a quartz vessel and was purified with respect to water and oxygen by heating the melt under vacuum and fusing it under argon. Indium trichloride was added through a lock-chamber. The voltammetric studies were carried out on an anodically polished tungsten working electrode (11).

All potentials were referred to the Ag/AgCl, NaCl-KCl half-cell reference (7).

Figure 1* shows a typical voltammogram. The sweep rate was 0.1 V.s⁻¹. The available domain of the melt is 2.4 V. The In(III) ions reduction to metallic indium follows two well-separated electrochemical steps:

- in the potential range +0.4 V to +0.16 V, the A/A' couple corresponds to the In(I)/In(III) exchange;
- in the potential range -0.475 V to -0.275 V, the B/B' couple is related to the In/In(I) exchange.

2. STUDY OF THE In/In(I) EQUILIBRIUM

We have verified that In(III) ions are completely reduced to monovalent indium by metallic indium according to the reaction:

\[ \text{In(III)} + 2 \text{In} \rightarrow 3 \text{In(I)} \]

The advancement of the reduction process was followed by measuring the indium liquid electrode potential; analyzes for In(I) by spectrophotometry of frozen melt samples were used to control the process.

The values of the electrode equilibrium potentials are reported in Table 2. A plot of potential vs. the logarithm of indium molar fraction yields a curve with a slope that fits a single electron transfer and gives the following for the apparent standard electrode potential:

\[ \varepsilon_x^{\text{In/In(I)}} : (-0.36 \pm 0.02) \text{ V / } \varepsilon_x^{\text{Ag/Ag(I)}} \]

*Editor's note: In the figure captions, E/R is used to designate the reference electrode.
3. REDUCTION MECHANISM OF THE TRIVALENT INDIUM IONS

3.1. The In(I)/In(III) Step

The In(I)/In(III) step was studied on a glassy carbon and on a gold electrode in trivalent indium chloride solutions.

Voltammetric experiments

Figure 2 presents two voltammograms related to the A/A' exchange. Curve A was obtained on a gold electrode and curve B on a glassy carbon one. The sweep rate was 4 V.s⁻¹. The shape of the curves is characteristic of a soluble-soluble transfer.

Owing to the high current flowing through the electrode, the voltammetric transients were altered by the ohmic drop interferences and were consequently analysed using convolution procedures (8,9).

The reversibility test was performed by comparing the semi-integral curves recorded at different sweep rates. We observed that the curves were very close and were the same during the forward and reverse scan. The semi-integral curve related to the voltammogram curve A of Figure 2 is shown in Figure 3. This behaviour proves that the electron exchange is very fast. The logarithmic transform of the

| Number of InCl₃ moles added  | Molar fraction of In(I) (spectrophotometric analysis) | Equilibrium indium electrode potential |
|-----------------------------|-----------------------------------------------------|---------------------------------------|
| 1.963 10⁻⁴                  | 8.60 10⁻⁵                                           | - 0.550 V                             |
| 2.313 10⁻⁴                  | 9.46 10⁻⁵                                           | - 0.538 V                             |
| 4.578 10⁻⁴                  | 1.84 10⁻⁴                                           | - 0.496 V                             |
| 6.040 10⁻⁴                  | 2.52 10⁻⁴                                           | - 0.438 V                             |
| 9.655 10⁻⁴                  | 3.90 10⁻⁴                                           | - 0.428 V                             |

Table 2 - In/In(I) equilibrium potential
semi-integral curve is shown in Figure 4. It follows that the electrode potential varies linearly versus \( \ln \left( \frac{m^* - m}{m} \right) \), where \( m \) is the semi-integral of the current density and \( m^* \) the cathodic limiting value of these functions obtained at high cathodic overpotentials, according to the Nernst relation:

\[
e = e^0 + \frac{RT}{2nF} \ln \frac{D_{\text{ox}}/D_{\text{red}}}{\ln \left( \frac{m^* - m}{m} \right)}
\]

The slope of the linear part of curve a in Figure 4 yields the number of the exchanged electrons:

\[
n = 2.1 \pm 0.1
\]

These results agree with the hypothesis that the \( A/A' \) couple is \( \text{In(I)}/\text{In(III)} \) and prove the reversibility of this couple.

**Chronopotentiometric experiments**

Figure 5 presents some chronopotentiometric transients obtained on a glassy carbon electrode. Only one transition is observed and the shape of the curve is characteristic of a soluble-soluble transfer.

The value \( iR^1/2/c \) remains constant when the current density is varied. Hence, the Sand relation is verified.

The logarithmic analysis of the chronopotentiograms (Figure 6) indicates a reversible soluble-soluble transfer (curve a) and an exchange of two electrons.

To summarize, we showed that the \( \text{In(I)}/\text{In(III)} \) exchange occurs reversibly on glassy carbon and gold electrodes. Finally, the apparent standard potential \( e_0' \text{In(I)}/\text{In(III)} \) was determined from the half peak potential of the convolution curves or from the quarter transition time potential. The trivalent diffusion coefficient of the indium ion was computed. The results are reported in Table 3.

| method of analysis        | \( e_{1/2} \) or \( e_{\tau/4} \) | \( D_{\text{In(III)}} \) (cm\(^2\cdot\text{s}^{-1}\)) |
|---------------------------|-----------------|------------------|
| Convolutional voltammetry | - 0.360 V       | \( (4.2 \pm 0.4) \times 10^{-5} \) |
| Chronopotentiometry       | - 0.356 V       | \( (4.5 \pm 0.6) \times 10^{-5} \) |

Table 3 - The apparent \( \text{In(I)}/\text{In(III)} \) standard potential, the \( \text{In(III)} \) diffusion coefficient.
3.2 The In/In(I) step

The In/In(I) step was studied on both tungsten and liquid-indium electrodes since glassy carbon and gold electrodes were not suitable.

The tungsten electrode reacts with the trivalent indium solutions but the kinetics is slow, and this electrode can be used for the study of the In/In(I) exchange. Figure 7 presents a voltammogram obtained on a tungsten electrode. The corresponding semi-integral curve is shown in Figure 8; two plateaus can be observed.

To obtain a reproducible behaviour with the liquid-indium electrode, it was necessary to proceed by chronopotentiometry with current reversal from a stationary oxidation state (10). Figure 9 presents a typical chronopotentiogram, corrected for the ohmic drop, obtained in the absence of indium species. The anodic and cathodic current densities were equal to 50 mA.cm\(^{-2}\).

The logarithmic analysis of the curve (Figure 10) indicates that the anodic pulse shape is characteristic of the metal oxidation. The following electrochemical step was postulated to explain departure from reversibility:

\[
\text{In} \rightarrow \text{In(III)} + 3e
\]

This electrochemical step is coupled to a slow chemical reaction:

\[
\text{In(III)} + 2 \text{In} \rightarrow 3 \text{In(I)}.
\]

Finally, the values deduced for the apparent standard In/In(I) potential are the same from voltammetric, chronopotentiometric, and equilibrium measurements (-0.38 V).
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Figure 1  Voltammetric study of a InCl$_3$ solution
Temperature : 700°C; electrolyte : 2.33 $10^{-2}$ molar InCl$_3$
solution;
working electrode : tungsten (area : 0.63 cm$^2$);
v $= 0.2$ V.s$^{-1}$; cycle : + 0.15 V $\rightarrow$ - 1.66 V $\rightarrow$ + 0.56 V/ER.

Figure 2  Voltammetric study of the In(I)/In(III) couple
Temperature : 700°C
a) working electrode : Gd (area : 1 cm$^2$)
electrolyte : 1.3.$10^{-2}$ molar InCl$_3$ solution ; v $= 4$ V.s$^{-1}$
cycle : + 0.45 V $\rightarrow$ + 0.24 V $\rightarrow$ + 0.48 V/ER
b) working electrode : glassy carbon (area : 0.65 cm$^2$)
electrolyte : 1.58.$10^{-2}$ molar InCl$_3$ solution ; v $= 4$ V.s$^{-1}$
cycle : + 0.45 V $\rightarrow$ - 0.24 V $\rightarrow$ + 0.48 V/ER
Figure 3  Convolutional analysis
Semi integral curve of the voltammogram a, figure 2

Figure 4  Logarithmic analysis
Analysis of the semi integral curve figure 3, according:
a) soluble-soluble hypothesis; b) soluble-insoluble hypothesis

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Figure 5  Chronopotentiometric study of the In(I)/In(III) couple

Temperature: 700°C; electrolyte: 1.06 $10^{-2}$ molar InCl$_3$; solution:
working electrode: glassy carbon (area: 0.65 cm$^2$); current density:
$\begin{align*}
|i| & : 1 : 0.021 \text{ A.cm}^{-2} ; 2 : 0.031 \text{ A.cm}^{-2} ; \\
3 : 0.038 \text{ A.cm}^{-2} 
\end{align*}$

Figure 6  Logarithmic analysis

Analysis of a chronopotentiogram (figure 5) according to:
a: the soluble-insoluble model; b: the soluble-soluble model
Figure 7  Voltammetric study of the In/In(I) couple
Temperature: 700°C; electrolyte: 2.6 \times 10^{-3} \text{ molar InCl}_3 solution; working electrode: tungsten (area: 0.63 cm²); 
v = 0.5 \text{ V.s}^{-1}
cycle: + 0.12 \text{ V} \rightarrow -0.58 \text{ V} \rightarrow +0.32 \text{ V} \rightarrow +0.12 \text{ V/ER}

Figure 8  Convolutional analysis
Semi integral curve of the voltammogram figure 7
Figure 9  Current reversal chronopotentiometry from a stationary oxidation state study

Temperature: 700°C; working electrode: indium (area: 1 cm²);

t = 2 s; |i₀| = |i| = 0.05 A cm⁻²

Electrolyte: NaCl-KCl equimolar solution, without InCl₃

Figure 10  Logarithmic analysis

Analysis of the anodic pulse according to the reversible hypothesis