CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Electrochemical Impedance Spectroscopy #3
Investigation of Indium(III) and Indium(I) in Fused LiCl-KCl at 450°C

Purpose

It has been shown by cyclic voltammetry (1) that $InCl_3$ in LiCl-KCl at 450°C undergoes two electron transfer reactions: a two-electron reduction to In(I), followed by a one-electron reduction to In(0), with the rate of the second electron transfer being slower than the first. The aim of this study was to confirm this mechanism using Electrochemical Impedance Spectroscopy (EIS).

Reference

Electrochemical Impedance Spectroscopy Study of Indium Couples in LiCl-KCl Eutectic at 450°C, M. Mohemedi, J. Bouteillon and J.C. Poignet, Electrochim. Acta 41 (1996) 1495-1504.

Method

EIS is a powerful method for investigating processes occurring at the electrode/electrolyte interface. Since a range of frequencies is used, processes occurring at different rates can be detected within one experiment.

Results

The cyclic voltammogram of a solution of $InCl_3$ in LiCl-KCl is shown in F1. Two couples can be seen: a two-electron process (Ia and Ic), corresponding to the In(III) + 2e = In(I) couple, and a one-electron process at more negative potentials (IIa and IIc), corresponding to the In(I) + e = In(0) couple. The two-electron couple was further investigated by recording the impedance spectrum at the equilibrium potential of a solution containing both In(III) and In(I) using either a tungsten or a glassy carbon working electrode. The Nyquist and Bode plots of the spectrum, obtained using the tungsten electrode, are shown in F2A and F2B, respectively. These are characteristic of diffusion-convection controlled electron transfer (the effect of electron transfer kinetics is not apparent in any of the plots). The magnitude of the diffusion layer for this type of mass transport control is independent of time. Therefore, at high frequencies, the spectrum is characteristic of semi-infinite diffusion (a straight line at 45° in the Nyquist plot, the phase angle approaching 45° in the phase angle *vs.*

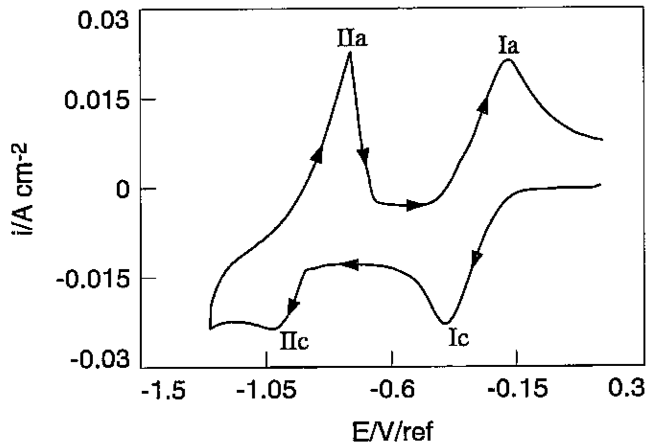

Figure 1. Cyclic voltammogram of $InCl_3$ in LiCl-KCl (5.75 mM) at 450°C at a glassy carbon electrode, scan rate = 0.9 V s^{-1}. All potentials measured with reference to Ag/AgCl. Figure adapted from primary reference.

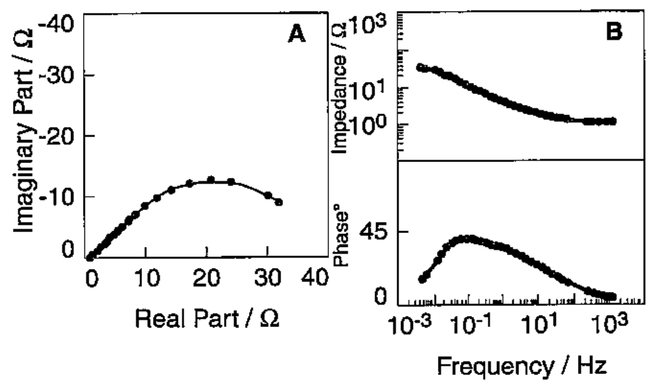

Figure 2. Nyquist plot (A) and Bode plots (B) obtained at the equilibrium potential of an LiCl-KCl solution of In(III) and In(I) (total In concentration = 33.6 mM) using a tungsten electrode. Points represent measured data, lines represent simulated data. Figure adapted from primary reference.

2701 Kent Ave • W. Lafayette,IN 47906 • (765) 463-4527 • FAX (765) 497-1102 • bas@bioanalytical.com

log frequency plot and a line of slope of 0.5 in the log Z *vs.* log frequency plot). However, as the wavelength of the A.C. potential becomes similar to thickness of the diffusion layer, the spectrum becomes characteristic of finite diffusion. Since the concentrations at the outer boundary of the diffusion layer are fixed, the characteristic behavior for this type of finite diffusion is resistive. Therefore, in the low frequency limit, the Nyquist plot intercepts the real axis, the phase angle tends to zero, and the slope of the log Z *vs.* log frequency plot approaches zero.

It should be noted that cylindrical tungsten and glassy carbon electrodes were used in this study rather than planar. As can be seen from the simulated impedance spectra in F3, this does not affect the spectrum at high frequencies, but low frequency behavior is significantly different for the two electrode geometries.

The impedance spectrum for the In(I)/In(0) couple was recorded at the equilibrium potential of a solution of In(I) in contact with a liquid In electrode (the In(I) was generated by electrochemical oxidation of the In electrode). The Nyquist and Bode plots are shown in F4A and B, respectively. The Nyquist plot is characteristic of electron transfer kinetic control at high frequencies (a semi-circle) with semi-infinite diffusion control at low frequencies (a straight line at an angle of 45°). This is indicative of moderate electron transfer kinetics (a rate constant of 3 x 10^{-2} cm s^{-1} was calculated from the charge transfer resistance, which is given by the difference of the two intercepts of the high frequency semi-circle with the real axis).

Reference

1) *J. Boutleillon, M. Jafarian, J.C. Poignet and A. Reydet, J. Electrochem. Soc. 139 (1992) 1*

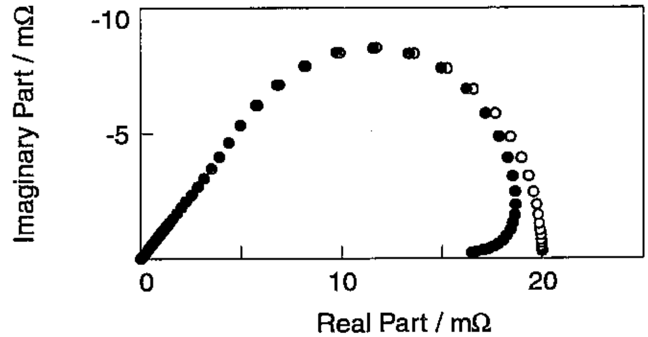

Figure 3. Comparison of the Nyquist plots of simulated impedance spectra for planar electrodes (white circles) and cylindrical electrodes (black circles) based on a convection-diffusion model. Figure adapted from primary reference.

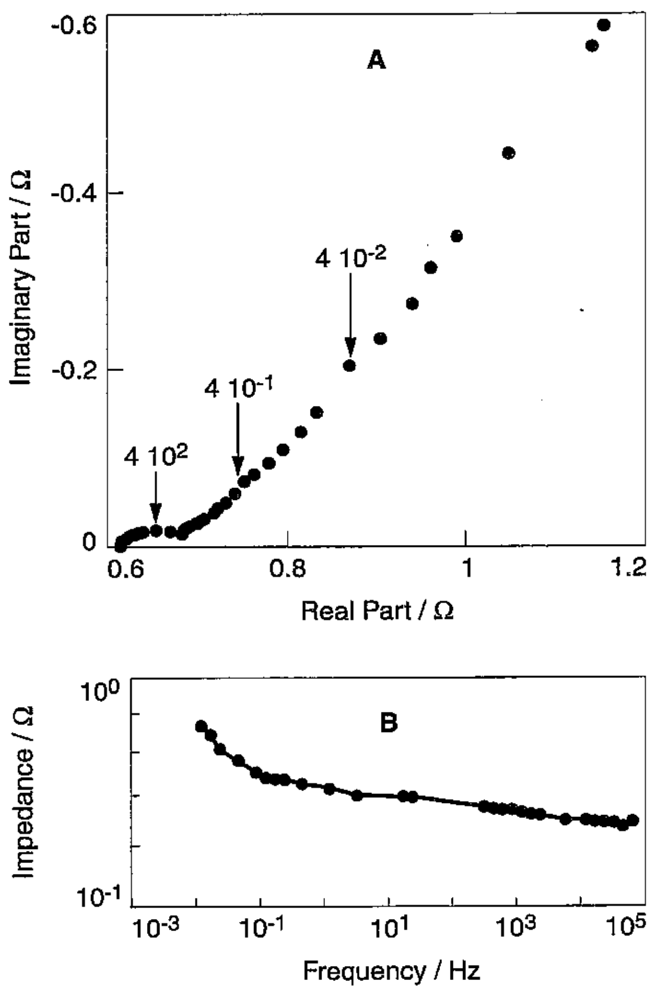

Figure 4. Nyquist (A) and Bode plots (B) obtained using an indium electrode in equilibrium with an LiCl-KCl solution of In(I). Figure adapted from primary reference.