Electrochemical behaviour of $Th^{4+}|Th$ couple in LiCl-KCl eutectic using electrochemical impedance spectroscopy

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Abstract

Electrochemical impedance spectroscopy (EIS) of $Th^{4+}|Th$ couple was carried out at inert tungsten (W) and liquid cadmium (Cd)electrodes in LiCl-KCl eutectic at temperature ranging 698 – 798 Ktoinvestigate the interfacial processes related with cathodic reduction of Th^{4+} ions. The impedance data were measured at different potentials and fitted to the equivalent circuits.

1. Introduction.

Reversibility of any redox couple depends on several electrode kinetics factors. Electrochemical impedance spectroscopy is best suited for estimating heterogeneous rate constant. The present work focuses on the equivalent circuit fitting of complex impedance spectra of $ThCl_4$ in LiCl-KCl eutectic at 773 K for determining charge transfer resistance, double layer charging capacitance etc and to study about kinetics and various interfacial processes occurring during reduction of Th^{4+} at inert as well as liquid Cd elctrodes in molten LiCl-KCl eutectic. Studies were carried out at both inert and liquid cadmium electrodes to compare the reduction behaviour of Th^{4+}. Elctrochemical behaviour of $Th^{4+}|Th$ couple has been investigated in molten salt earlier by various groups. Only one stable oxidation state +4 of thorium ion was found in molten LiCl-KCl eutectic and reduction of Th^{4+} to Th metal was found one step four electron transferred process by Gurudas et al. [1] and Cassayre et al. [2] using cyclic voltammetry method. The authors [1,2] also have measured various electrochemical properties likeDiffusion coefficient (D), charge transfer coefficient (α), activation energy (E_a), apparent standard reduction potential (E^{0*}) of $Th^{4+}|Th$ couple in molten LiCl-KCl eutectic at inert electrode using various transient electrochemical techniques like cyclic voltammetry, chronopotentiometry, square wave voltammetry etc.

2. Experimental

2.1. Chemicals: All chemicals used in present work were of analytical grade. Anhydrous lithium chloride was obtained from Alfa Aesar (Ã 98%), anhydrous potassium chloride was obtained from Ranbaxy Fine Chemicals, India. Cadmium chloride, anhydrous (Ã99.9%) was obtained from Alfa Aesar. Cadmium shots (Ã99.95%) of 3 mm diameter were obtained from Arora Matthey, Kolkata. Thorium metal was obtained from BhabhaAtomic Research Centre, Mumbai.

2.2. Preparations of electrolyte and electrode: LiCl-KCl-$ThCl_4$ electrolyte was prepared by equilibration of thorium metal with cadmium chloride in molten LiCl-KCl eutectic inside an alumina crucible at 773 K for 30 h inside Ar atmosphere glove box. Liquid cadmium electrode was prepared by dropping cadmium shots (20 g) into an alumina crucible placed inside a SS perforated basket and immersed in molten LiCl-KCl eutectic at 773 K.

3. Results

3.1. Analysis of electrochemical impedance data of LiCl-KCl-ThCl4 system

The electrochemical impedance spectra of $Th^{4+}|Th$ couple were recorded at different cathodic potentials in the range of -0.8 V to -1.55 V *vs.* Ag/AgCl reference at inert Wand liquid Cd electrodesin the frequency range between 10 Hz to 10 kHz at 773 K for $ThCl_4$ in molten LiCl-KCl eutectic. After each measurement a cyclic voltammogram was recorded in order to control

the state of the electrolyte and electrodes. The impedance spectrums were fitted to equivalent circuits in the frequency range of 10 Hz to 10 kHz. Resistor elements R_1 andR_2 corresponding to electrolyte resistance and charge transfer resistance respectively, constant phase element (CPE or Q), capacitance (C) and Warburg impedance (W) were used for fitting the equivalent circuit.

$$k_s = \frac{RT}{R_{CT} n^2 F^2 C^{1-\alpha}} \qquad (1)$$

Figure 1 show typical electrochemical impedance spectra of Th^{4+}|Th couple recorded in the potential range of -0.8 V to -1.5 V*vs.* Ag/AgCl reference at inert tungsten (W) electrode at 773 K. Impedance data measured at -0.8 V (Fig 1a) was subsequently fitted to an equivalent circuit containing two parallel CPE elementsin series with a resistor R_1. This potential corresponds to the diffusion of and also adsorption of Th^{4+} ions. One of the CPE was interpreted to be related to diffusion controlled process where n 4 0.5 (Warburg impedance) and another CPE was

interpreted to be related to adsorption phenomena where n 4 1 (capacitance dominated) as discussed by Reddy *et al*. [3]. Impedance data measured at -1.4 V (Fig. 1b) was fitted into an equivalent circuit containing one CPE in series with a resistance element R_2 and one capacitor C_1 in parallel with these two. From circuit fitting resistance R_2 was found to be 0.293 ± 0.13 Ω. Heterogeneous rate constant k_s was calculated to be 3.54 x 10^{-5} cm s^{-1} at -1.4 Vusing equation 1.Charge transfer process was rapid at this potential as R_2value was minimum. Charge transfer process was accompanied by diffusion of Th^{4+} ions. CPE was interpreted to be diffusion controlled process as n 4 0.5 was found. Measured impedance data at -1.5 V (Fig 1c) was fitted into an equivalent circuit which contains one CPE is in series with a resistance element R_2. The CPE and resistance element correspond to diffusion and Th^{4+} and charge transfer of Th^{4+} to Th metal respectively.

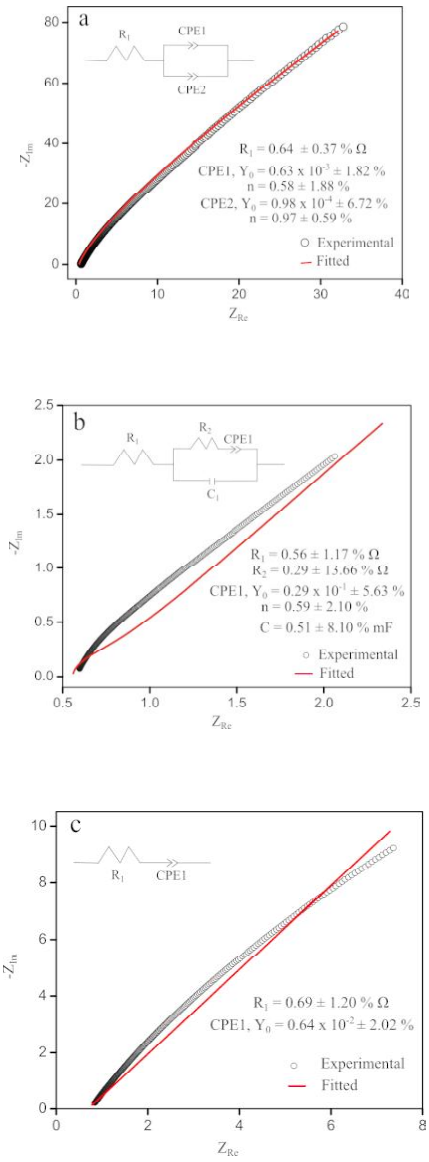
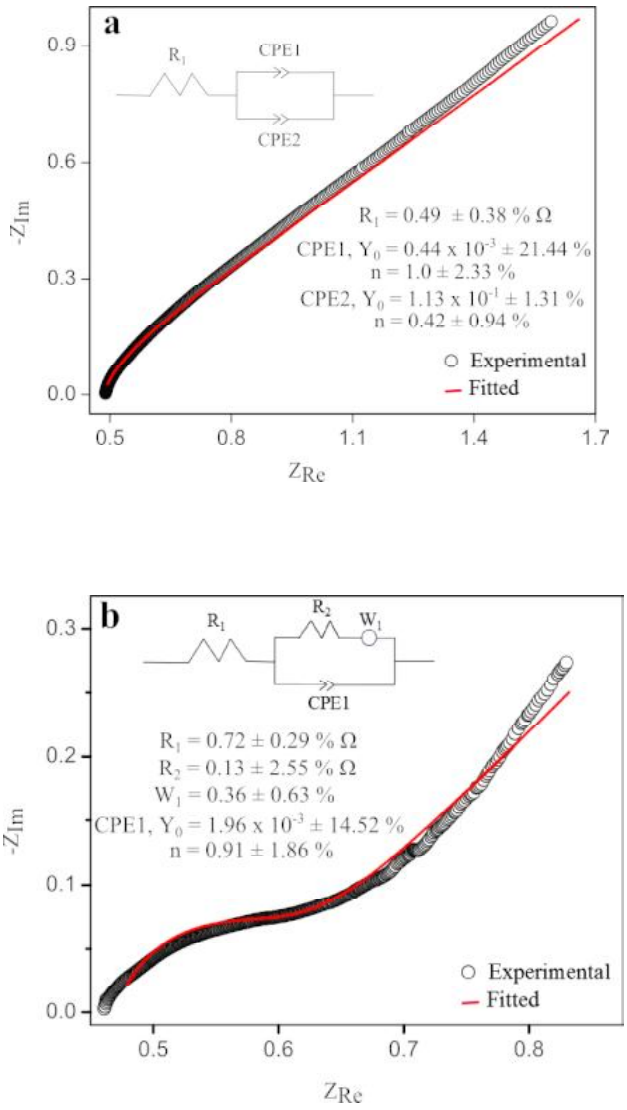


Figure 1: Complex impedance spectra of $ThCl_4$ in molten LiCl-KCl eutectic at W electrode at applied potential (a) -0.8 V, (b) -1.4 V, (c) -1.5 V at 773 K.

In the same way impedance spectra of Th^{4+}|Th couple in molten LiCl-KCl eutectic were recorded at liquid cadmium electrode at three different potentials ranging -0.8 V to -1.4 V *vs.* Ag|AgCl reference, at OCP (No redox reaction), low and high cathodic potentials respectively at 773 K.Impedance spectra recorded at -0.8 V, -1.1 V and -1.4 V are shown in figure 2.Impedance data recorded at -0.8 V (Fig 2a) shows similar trend to figure 1a. Impedance data recorded at -1.1 V and -1.4 V shown in figures 2b and 2c respectively

was fitted to an equivalent circuit containing Warburg impedance in series with a resistance element R_2 and one constant phase element in parallel with these two. Charge transfer rate was observed to be maximum at -1.2 V as minimum value (0.042 ± 0.067 Ω) of R_2 was found at this potential.



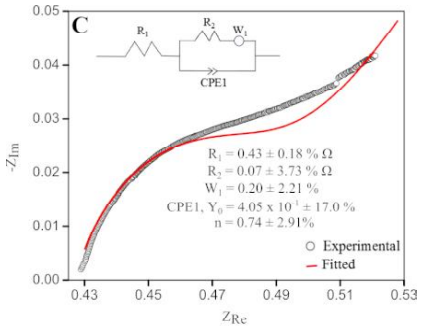


Figure 2: Complex impedance spectra of $ThCl_4$ in molten LiCl-KCl eutectic at liquid Cd electrode at applied potential (a) -0.8 V, (b) -1.1 V, (c) -1.4 V at 773 K.

4. Conclusion: The study was performed to investigate the electrochemical deposition behaviour of Th^{4+} ions at inert and liquid Cd cathodes employing impedance spectroscopy. It was observed that impedance response at OCP for both inert and liquid Cd electrodes was related to diffusion and adsorption of Th^{4+} ions. At low cathodicpotential a semicircle was observed at lower frequency range which infers slow charge transfer rate but at higher cathodic potential the disappearance of the semicircle infer the rapid charge transfer rate at electrode-electrolyte interface.

References:

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