

## A Cyclic Voltammetric Study of Lithium Conducting Vitreous Solid Electrolytes

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Foram realizados estudos por voltametria cíclica em dois eletrólitos sólidos vítreos condutores por íon lítio a fim de se determinar o seu domínio de estabilidade de óxido redução. O primeiro eletrólito, de composição  $0,40\text{Li}_2\text{O} \cdot 0,20\text{B}_2\text{O}_3 \cdot 0,40\text{P}_2\text{O}_5$  apresenta em seu voltamograma apenas as reações de redução e oxidação do par  $\text{Li}^+/\text{Li}$ . O segundo, dopado com  $\text{LiCl}$   $0,8(0,40\text{Li}_2\text{O} \cdot 0,20\text{B}_2\text{O}_3 \cdot 0,40\text{P}_2\text{O}_5)0,2\text{LiCl}$  mostra um domínio de estabilidade reduzido pela oxidação dos íons cloretos. O número de transporte aniônico foi calculado para o vidro dopado, sendo igual a  $5,0 \times 10^{-4}$ .

Cyclic voltammetric studies were performed on two lithium conducting vitreous solid electrolytes to determine their stability domain. The first one, with a  $0.40\text{Li}_2\text{O} \cdot 0.20\text{B}_2\text{O}_3 \cdot 0.40\text{P}_2\text{O}_5$  composition showed no reaction in the voltammetric curve other than a  $\text{Li}^+/\text{Li}$  reduction. The second electrolyte, doped with  $\text{LiCl}$ ,  $0.8(0.40\text{Li}_2\text{O} \cdot 0.20\text{B}_2\text{O}_3 \cdot 0.40\text{P}_2\text{O}_5)0.2\text{LiCl}$  presented a stability slightly reduced by chloride oxidation. An anionic transport of  $5.0 \times 10^{-4}$  was determined for the doped glass.

**Keywords:** solid electrolytes, lithium conduction, conductive glasses

### Introduction

The broad applicability of and recent advances made in lithium batteries makes the search for lithium conducting solid electrolytes a focus of great interest since the total performance of such batteries is directly linked to characteristics of the electrolyte.

In order to guarantee good battery performance, it is necessary for the electrolyte possess certain properties, such as high ionic conductivity, the absence of electronic conductivity, and a redox stability range compatible with the electrodes being used. It is also desirable for the conductivity to be predominantly cationic thereby reducing the formation of dendrites or parasitic reactions on the anode deriving from anion conduction.

In comparison with liquid electrolytes, solid electrolytes have the advantage of not presenting leakage problems. Among solid electrolytes, the main advantage of vitreous electrolytes, principally in comparison to polymeric ones, is that they exhibit exclusively cationic conduction. In relation to crystalline solids, the amorphous nature of glass implies facilitated ionic conduction. Batteries using vitreous solid electrolytes have already been studied<sup>1</sup> and have even been made commercially available<sup>2</sup>.

In this work, two vitreous solid electrolytes are presented, the first being composed of  $0.40\text{Li}_2\text{O} \cdot 0.20\text{B}_2\text{O}_3 \cdot 0.40\text{P}_2\text{O}_5$ , which is called non-doped or base-glass. With the aim of increasing the conductivity of this electrolyte,  $\text{LiCl}$  was added to the existing glass resulting in a new material with the composition  $0.8(0.40\text{Li}_2\text{O} \cdot 0.20\text{B}_2\text{O}_3 \cdot 0.40\text{P}_2\text{O}_5)0.2\text{LiCl}$ , called doped glass.

Cyclic voltammetric studies allowed the determination of the redox stability range in both electrolytes, as well as the determination of the anionic transport number in the doped one.

## Experimental

### Sample preparation

The base-glass was prepared by melting the mixture of the calculated quantities of anhydrous  $\text{Li}_2\text{CO}_3$ ,  $\text{B}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  in a platinum crucible heated by the Joule effect at a temperature of  $1100\text{ }^\circ\text{C}$ , and the liquid was then poured into a cylindrical mold at room temperature. The doped glass was obtained by adding anhydrous  $\text{LiCl}$  to the ground base-glass, the mixture re-melted at  $900\text{ }^\circ\text{C}$ , and then poured into a mold pre-heated to the annealing temperature. This annealing, necessary for the relaxation of the internal stresses in the glass, was carried out at  $50\text{ }^\circ\text{C}$  below the glass transition temperature,  $T_g$  ( $T_g$  base-glass =  $400\text{ }^\circ\text{C}$ ;  $T_g$  doped glass =  $330\text{ }^\circ\text{C}$ , measured by differential scanning calorimetry, with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ ).

### Electrical characterization

The electrical conductivity of the glasses being studied was determined by impedance spectroscopy in the 5 Hz to 13 MHz frequency range, using gold as the contact electrode<sup>3</sup>. The measurements were carried out between room temperature and  $200\text{ }^\circ\text{C}$ .

### Cyclic voltammetry

Cyclic voltammetric studies were carried out in the cell shown in Fig. 1. The sample being studied, or electrolyte, is a cylinder with a 13 mm diameter and 2 mm of thickness. The working electrode, (W.E.), consisted of a layer of gold deposited by cathodic pulverization. The counter electrode, (C.E.), was a layer of silver, in the form of a ring, also deposited by cathodic pulverization. The reference electrode, (R.E.) was an  $\text{Ag}/\text{Ag}_3\text{SI}$  electrode<sup>4,5</sup>, placed in the center of the sample, on the side where the C.E. was deposited, the contact being achieved by simple pressure. The measurement cell was placed inside an oven (Buchi TO-50), ensuring working temperatures in the range of  $25\text{--}200\text{ }^\circ\text{C}$ . The electrical equipment included a Tacussel PRT-40-IX potentiostat controlled by a GSTP generator.

## Results and Discussion

The base-glass exhibited electrical conductivity at  $100\text{ }^\circ\text{C}$ ,  $\sigma_{100\text{ }^\circ\text{C}} = 1.16 \times 10^{-6}\text{ }(\Omega\text{cm})^{-1}$ , and a conduction activation energy equal to  $0.63\text{ eV}$ . The introduction of  $\text{LiCl}$  into the macromolecular chain of glass causes an increase in the number of charge carriers ( $\text{Li}^+$ ), resulting in higher ionic conductivity and lowering the activation energy. The doped glass under study exhibited electrical

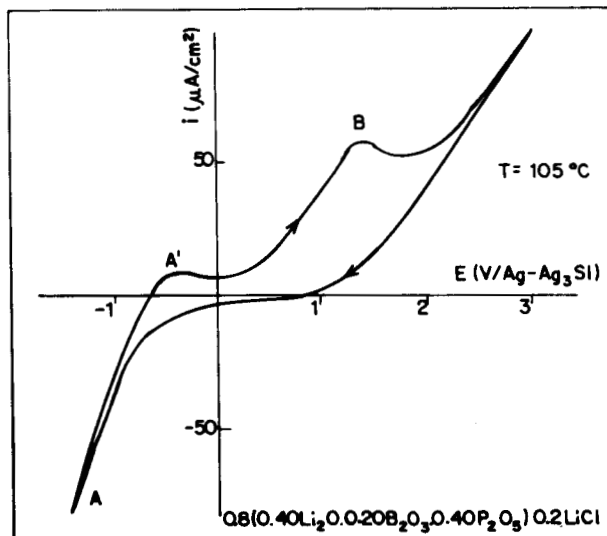


Figure 1. Scheme of the cell used for cyclic voltammetric measurements.

conductivity at  $100\text{ }^\circ\text{C}$ ,  $\sigma_{100\text{ }^\circ\text{C}} = 3.48 \times 10^{-5}\text{ }(\Omega\text{cm})^{-1}$ , and a conduction activation energy equal to  $0.51\text{ eV}$ .

Figure 2 represents the first cycle of the voltammetric curve obtained from the base-glass. The experiment was carried out at  $140\text{ }^\circ\text{C}$  under vacuum, to prevent any interference from ambient oxygen or humidity. In A, during the cathodic sweep, the reduction of lithium is observed, which becomes re-oxidized in A' according to the reaction  $\text{Li} \rightleftharpoons \text{Li}^+ + \text{e}^-$ . In the anodic region, for potentials higher than  $-1\text{ V}$ , no oxidation process was observed for potentials up to  $3\text{ V}$ . The width of the redox stability range is therefore higher than  $3\text{ V}$ , with a current density of  $0.01\text{ mA}/\text{cm}^2$ .

Figure 3 shows the first cycle of the voltammetric curve obtained at  $105\text{ }^\circ\text{C}$  for doped glass, which was carried out in conditions analogous to those of the previous case. In A and A', the reduction and oxidation of the  $\text{Li}/\text{Li}^+$  pair was respectively identified.

The current density at  $-1\text{ V}$  in Fig. 3 is slightly higher than in Fig. 2, despite the lower working temperature. This response could be associated with the higher lithium content of the doped glass. The  $\text{Li}^+$  reduction is irreversible due to the reaction between lithium and the gold from the working electrode, probably forming an intermetallic compound. As such, at  $1\text{ mV}/\text{s}$ , only about 10% of the cathodic charge is recovered in the anodic sweep until  $0\text{ V}$ .

By analogy with the studies carried out on silver glass conductors doped with alkaline halogens<sup>6</sup>, we can attribute peak B in Fig. 3 to the oxidation of the chloride ions:  $\text{Cl}^- \rightleftharpoons 1/2 \text{Cl}_2 + \text{e}^-$ . This peak is found at approximately  $1.65\text{ V}/\text{Ag}_3\text{SI}$ . A reduction peak of the chlorine is not observed in the cathodic sweep, since any chlorine formed is evacuated by the vacuum pump.

It should be noted in this case that the redox stability range is reduced by the oxidation of the chloride anions, which oxidize much more easily than the anions of the macromolecular glass chain, resulting in a redox stability

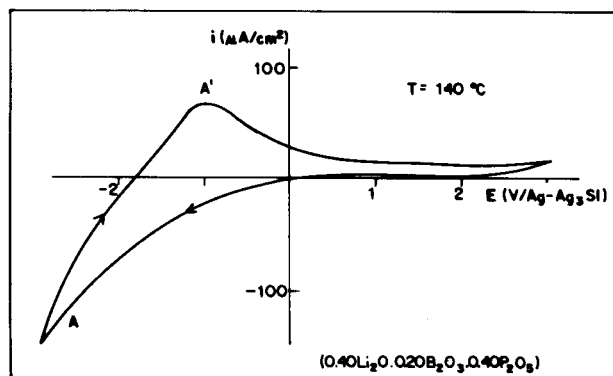


Figure 2. Voltammetric curve of the base-glass obtained with a sweep rate of 1mV/s.

range on the order of 1.4 V, with a current density of 0.01 mA/cm<sup>2</sup>.

With the aim of calculating the diffusion coefficient of the chloride ions, the equation proposed by Delahay<sup>7</sup> was used. This equation relates peak intensity to the sweep rate for the electroactive species, whose transport is limited by diffusion:

$$I_p = \frac{0.452n^{3/2}F^{3/2}}{R^{1/2}T^{1/2}} D_x^{1/2}[X]v^{1/2}$$

where:  $I_p$  = peak intensity;  $D_x$  = diffusion coefficient of the species X;  $[X]$  = concentration of species X;  $v$  = sweep rate; and  $F$ ,  $R$ ,  $T$  and  $n$  have their usual meanings.

From this equation, as well as from the intensity of the peak observed on the voltammogram and the concentration of the chloride ions provided by density measurements<sup>3</sup>, we can estimate the diffusion coefficient of the chloride ions in the glass. The calculations result in:  $D_{Cl^-} = 8.6 \times 10^{-13}$  cm<sup>2</sup>/s.

In the absence of electronic conductivity, and if the mobility of the species is the same with or without an electrical field, the Nernst-Einstein equation for self-diffusion in solids relates the partial conductivity ( $\sigma_{Cl^-}$ ) to the total conductivity ( $\sigma_t$ ) and the diffusion coefficient of the mobile species<sup>8</sup>.

Thus:

$$\sigma_{Cl^-} = \frac{D_{Cl^-}[Cl^-]Z^2\sigma_t^2}{RT}$$

from which  $\sigma_{Cl^-} = 2.0 \times 10^{-8}$  ( $\Omega\text{cm}$ )<sup>-1</sup> at 105 °C, thereby obtaining the anionic transport number:

$$t_{Cl^-} = \frac{\sigma_{Cl^-}}{\sigma_t} \cong 5.0 \times 10^{-4}$$

showing that the conduction by chloride ions is negligible in relation to the conduction by lithium ions.

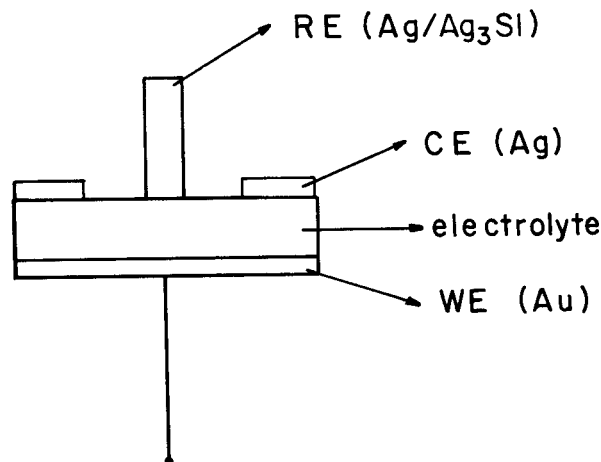


Figure 3. Voltammetric curve of the LiCl doped glass. Sweep rate = 1mV/s.

## Conclusion

The non-doped glass, 0.40Li<sub>2</sub>O.0.20B<sub>2</sub>O<sub>3</sub>.0.40P<sub>2</sub>O<sub>5</sub>, does not present in the voltammetric curve any reaction other than that of lithium oxidation. The redox stability range of this solid glassy electrolyte is compatible with use in a lithium battery. The glass doped with LiCl has its redox stability range reduced by the oxidation of the chloride anions. For this sample, it was possible to calculate, by means of the voltammetric curve obtained, the anionic transport number  $t_{Cl^-} = 5.0 \times 10^{-4}$ , demonstrating that conduction occurs predominantly through the lithium ions.

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