Ionic Conductivity of Chitosan-Lithium Electrolyte in Biodegradable Battery Cell

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Abstract: *The electrical conductivities of salts (LiCl, LiOH) in chitosan as an electrolyte in biodegradable batteries have been measured at the concentration range 10–100 mol m^{-3} in the temperature range 278–308 K. The data were interpreted in terms of ion–ion and ion–solvent interactions using the Fuoss paired ion. The fitting of Fuoss' equation of 1978 to these data led us to an estimate of the ionic association by computing the conductimetric pairing constants. In order to optimize the use of the electrolyte in the clean lithium battery, the temperature dependency of conductivity will be studied using Arrhenius empirical equation. This equation was applied successfully in the temperature range used in this study.*

■ INTRODUCTION

In recent years, the development of polymer electrolytes has been a central challenge to be faced by academic and industrial interests [1-2]. These materials have vast potential applications in various electrochemical devices [3-5]. They offer many advantages under liquid electrolytes, such as no internal shorting, leakage of electrolytes and non-combustible reaction products at the electrode surface existing in the liquid electrolytes [6]. Chitosan has been under extensive research on account of its specific properties, such as being non–toxic and biodegradable and also because of its promising potential in biomedical, pharmaceutical, and industrial applications [7-8]. Chitosan also constitutes a polymer host for electrolyte as it is able to dissolve ionic salts [9].

Electrical conductivity, the most vital electrolyte properties of chitosan, can be increased by several methods. Rosli et al. [10] studied the effect of TiO$_2$ filler on the structure and electrical properties of hexanoyl chitosan/polystyrene based electrolytes. The conductivity for filler-free polymer electrolyte is 7.21×10^{-5} S cm^{-1}. The addition of 4 wt.% TiO$_2$ increased the conductivity by one order of magnitude to 2.27×10^{-4} S cm^{-1}. Yulianti et al. [11] have successfully studied Ion Implantation Technique to prepare a solid-state electrolyte based on chitosan. Various ion salts (Li, Cu, Ag) was involved in the chitosan matrix. The results show that after implanted with Li, Cu or Ag ion, the conductivity of chitosan film increased significantly. Traditional lithium salts used in polymer electrolytes are LiPF$_4$, LiClO$_4$, LiBF$_4$, etc.

Up to now the lithium – ion batteries used specific electrolytes LiPF$_4$, LiPF$_6$, etc., dissolved in organic solvents such as Propylene Carbonate (PC) Acetonitrile (AN), etc. Our goal in this research is to substitute the toxic solvents (PC, AN) by the biodegradable and non-toxic solvent "Chitosan", with a view to elaborate a lithium-ion battery based on this clean and biodegradable solvent. We find it interesting to make measurements of conductivity with a lithium salt. This is performed in order to optimize the electrolyte composition to be used in a clean lithium battery without the use of toxic solvents like Propylene Carbonate (PC) and Acetonitrile (AN). The experimental conductance data will be analyzed by the known equations of the literature namely the Fuoss equation of 1978, Casteel–Amis empirical equation and Arrhenius empirical equation for the temperature dependence of the conductivity.

■ EXPERIMENTAL SECTION

Electrolytes with lithium salts, lithium chloride (LiCl) and Lithium hydroxide (LiOH) were prepared with distilled water and Chitosan. The LiCl and LiOH salts had a purity grade of 99.5% and 99%, respectively. The initial solution concentration for each electrolyte was prepared by weight using the electronic balance Ohaus As200. For the electrolyte solution, the concentrated solution was obtained by simply adding the necessary mass of lithium salts to the previous solution. Depending on its mass, lithium salts will require a period between 1–4 h to be completely dissolved using a magnetic stirrer. To prepare the polymer electrolyte, 0.5 g of chitosan was dissolved in 50 mL of acetic acid at 3% vol/vol. For the desired concentration, the lithium salt was added, and the mixture was placed in a magnetic stirrer at 313 K for 18 h. All prepared solutions were covered by paraffin.

The conductivity measurements were carried out using the EC215 conductivity meter (Hanna Instruments) having a resolution of 0.01 μS cm^{-1}, a precision of 1% and an automatic correction of temperature shift during the measurement. Before use, the instrument was calibrated using the standard KCl solution HI 7031. The solution was placed into a special dual wall cell suitable for temperature control and connected to the cryostat (Lauda RE1050- CP) filled with ethylene glycol where the desired temperature was kept constant (Fig. 1).

Theoretical Equations

Fuoss's model

According to Fuoss's paired ion model, an equilibrium may be established through the following reaction [12]:

$$A^+ + B^- \leftrightarrow \left(A^+{\cdots}B^-\right) \leftrightarrow \left(A^+B^-\right) \leftrightarrow (AB)$$
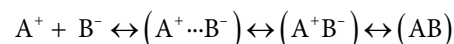
A$^+$ and B$^-$ are free ions; (A$^+{\cdots}$B$^-$) are solvent separated pairs; (A$^+$B$^-$) are contact pairs and (AB) are neutral molecules.

In this theory, the effects of ion–ion and ion–solvent interactions enter through two adjustable parameters, the parameter α and Gurney radius (R$_g$). The parameter Rg is the radius of the spherical portion of the solvent that encloses the ion. The parameter (α) is a fraction defined by
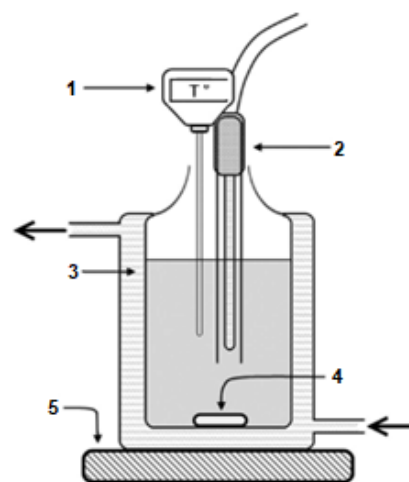
Fig 1. Experimental diagram. 1: Thermometer; 2: Electrical conductivity probe; 3: Heat-transfer fluid (Ethylene glycol); 4: Magnetic stir bars; 5: Magnetic stirrer

classifying each ion according to the magnitude of r, the distance from the center of the ion to that of the nearest neighbor of opposite sign. If r > R, then the ion is unpaired, otherwise the ion is said to be paired. If r << R, the paired ion and its neighbor constitute a contact pair which does not contribute to the conduction process. The experimental data were analyzed using Fuoss' conductance equation, expressed as:

$$\Lambda = P\left[\Lambda_0(1+RX)+EL\right] \tag{1}$$

$$P = 1 - \alpha(1-\gamma) \tag{2}$$

$$\gamma = 1 - K_A C\gamma^2 f^2 \tag{3}$$

$$-\ln f = \frac{\beta\kappa}{2(1+\kappa R)} \tag{4}$$

$$\beta = \frac{e^2}{\varepsilon k_b T} \tag{5}$$

$$K_A = K_R(1+K_S) \tag{6}$$

In these equations, R represents the Gurney radius; γ the fraction of unpaired ions (free ions); p the fraction of solvent-separated pairs; α the fraction of contact pairs; K$_A$ the overall pairing constant evaluated from the association constant of contact-pairs (K$_S$) and the association constant of solvent-separated pairs (K$_R$). The variables f, β, and κ have their usual meanings; RX (relaxation effect) and EL (electrophoresis effect) are parameters depending on the physical properties of the solvent and the temperature, given, in SI units, by:

$$RX = \frac{-\beta\kappa}{6(1+1/\sqrt{2})(1+t)(1+t/\sqrt{2})} + \frac{\beta^2\kappa^2}{12}\ln t + \beta^2\kappa^2 FH2$$
$$+\beta^3\kappa^3 FH3 + [\frac{\beta_0 C^{1/2}\gamma^{1/2}}{\Lambda_0}]\,(\frac{\beta\kappa}{8})\,[0.5H2-\ln t] \quad (7)$$

$$EL = -\beta_0 C^{1/2}\gamma^{1/2}[\frac{1}{1+t} + \beta\kappa(0.125\ln t) + 0.5H1] \quad (8)$$

$$\beta_0 = \frac{Fe\kappa}{3\pi\eta C^{1/2}} \quad (9)$$

$$t = \kappa R \quad (10)$$

FH2, FH3, H1, and H2 are the interpolation polynomials introduced by Fuoss in order to facilitate solving the equation of conductance [12].

The method was used as follows: In our computer program, we used the interpolation polynomials established by Fuoss based on its model of ion pairs (1978) Eq. (1-10). In our case, we have adopted the method of calculation mentioned below. Indeed, we worked with the molar conductivity value at infinite dilution Λ_0 graphically obtained by extrapolation using the Debye-Huckel limiting law-Onsager. Indeed, for each electrolyte and for each concentration, we used a simple method to reproduce the experimental data of conductivity. Afterwards, we set an arbitrary value of α and varied the value of R_g until a standard deviation of σ is minimum, Eq. (11). Then, we fixed the value of R_g and varied the value of α until a minimum standard deviation σ was obtained to vary the radius of Gurney (R_g), by setting an arbitrary value of (α). Finally, we deduced the remaining Fuoss's parameters already described: molar conductivity at infinite dilution (Λ_0), the fraction (α) and the association constant (K_A). The calculated value was compared to the measured value of (R_g) and (α), seeking the minimum standard deviation:

$$\sigma^2 = \frac{\sum\left(\Lambda_{J(cal)} - \Lambda_{J(obs)}\right)^2}{n-2} \quad (11)$$

n is the number of concentrations used during the experiment.

Casteel-Amis empirical model

To describe the relationship between the electrical conductivity with concentration, the empirical Castel-Amis equation was used [13]. The empirical equation was written as follows:

$$\kappa = \kappa_{max}\left(\frac{C}{C_{max}}\right)^a \exp\left[b\left(C-C_{max}\right)^2 - \frac{a}{C_{max}}\left(C-C_{max}\right)\right] \quad (12)$$

In this equation, C_{max} is the concentration at which the specific conductivity maximum κ_{max} is attained. The constants (a) and (b) are arbitrarily chosen and adjusted by the least-squares method.

Arrhenius equation

On the basis of transport theory of solutions, we use the Arrhenius type temperature conductivity, which can be written as [14]:

$$\kappa = A\exp(\frac{E_a}{k_B T}) \quad (13)$$

where $A = \kappa_\infty$ represents the maximum electrical conductivity at infinite temperature, E_a is the activation energy for ionic conduction and k_B is the Boltzmann constant.

■ RESULTS AND DISCUSSION

The variation of the molar conductivity data for LiCl and LiOH in chitosan were analyzed by Fuoss, while the specific conductivity data were analyzed using the Casteel–Amis equation. These data are given in Table 1.

Table 1. Molar conductivities Λ of LiOH and LiCl in chitosan at 298 K

C	Λ LiOH	Λ LiCl
(mol m^{-3})	(S m^2 mol^{-1})	(S m^2 mol^{-1})
10	0.220	0.135
20	0.205	0.120
30	0.200	0.116
40	0.192	0.112
50	0.190	0.112
60	0.186	0.110
70	0.185	0.107
80	0.184	0.106
90	0.183	0.105
100	0.182	0.104

Table 2. Fuoss' parameters Λ_0, α, R and K_A for LiOH and LiCl in chitosan at 298 K
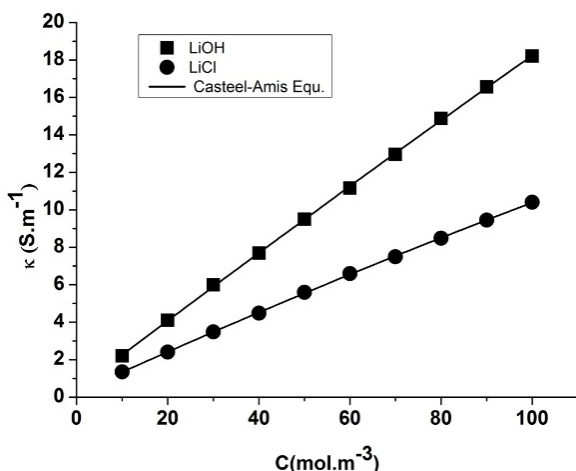
	Λ_0	α	R	K_A
	(S m^2 mol^{-1})		(nm)	(m^2 mol^{-1})
LiOH	0.139	0.3	0.85	2.8×10^{-3}
LiCl	0.235	0.45	0.65	6.2×10^{-3}
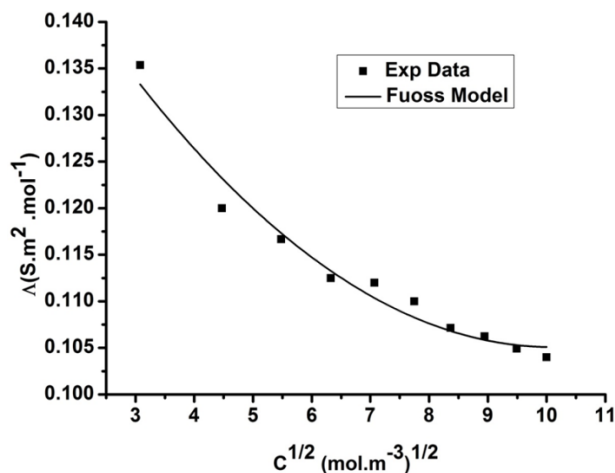
Fig 2. Molar conductivity of LiCl in chitosan versus $C^{1/2}$ at 25 °C. The solid line represents the Fuoss conductance equation
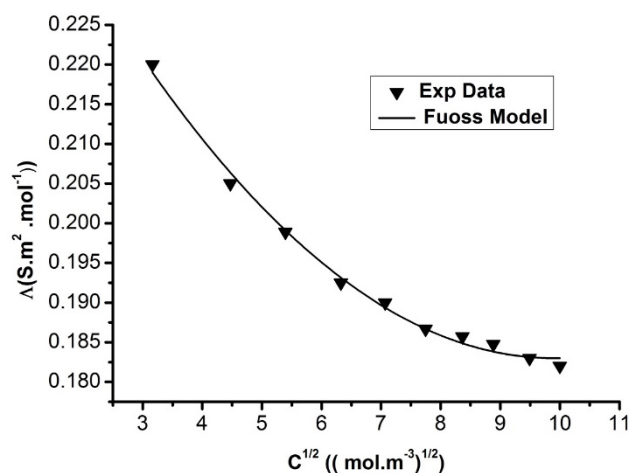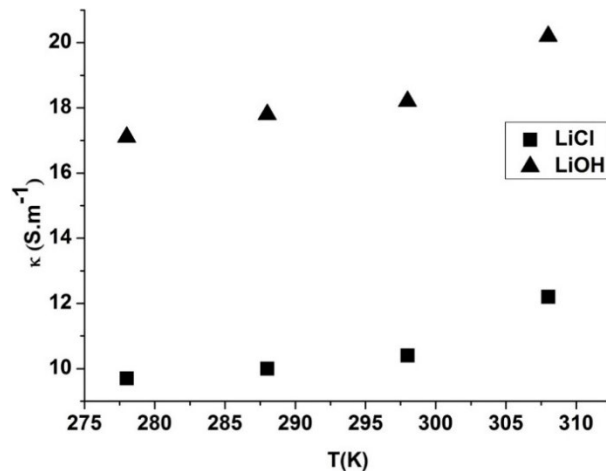

Fig 3. Molar conductivity of LiOH in chitosan versus $C^{1/2}$ at 25 °C. The solid line represents the Fuoss conductance equation

The molar conductivities are plotted against the square root of the salt concentration according to the model of Fuoss in Fig. 2 and 3. As can be seen in these figures, the molar conductivity decrease when the square root of the concentration increase. The solid line was calculated using equation 1 in the model of Fuoss. Values of Λ_0, α, R and K_A obtained by this method are listed in Table 2.

The conductivity data (κ) for two electrolytes were analyzed using the semi-empirical Casteel-Amis equation. They are plotted in Fig. 4. The values of the parameters C_{max}, κ_{max}, a and b are given in Table 3.

The value of (b) tends to be small and negative in all systems and seem to be influenced by dielectric constant. This result was previously found for LiCl in glycerol [15]. However, the coefficient (a) was all positive

**Table 3.** Casteel–Amis parameters κ_{max}, C_{max}, a and b for LiOH and LiCl in chitosan

	κ_{max} (S m^{-1})	C_{max} (mol dm^{-3})	a	b
LiOH	126.9	1420	1.12	-0.55
LiCl	32.9	590	1.01	-0.45

Fig 4. The specific conductance κ as a function of concentration C of LiOH and LiCl in chitosan at 298 K

Fig 5. The specific conductance κ as a function of temperature T of LiOH and LiCl in chitosan

Table 4. The conductivities κ of LiCl and LIOH in chitosan in the temperature range 278–308 K

K (S m^{-1})	T = 308 K	T = 298 K	T = 288 K	T = 278 K
LiOH	20.2	18.2	17.8	17.1
LiCl	12.2	10.4	10.0	9.7
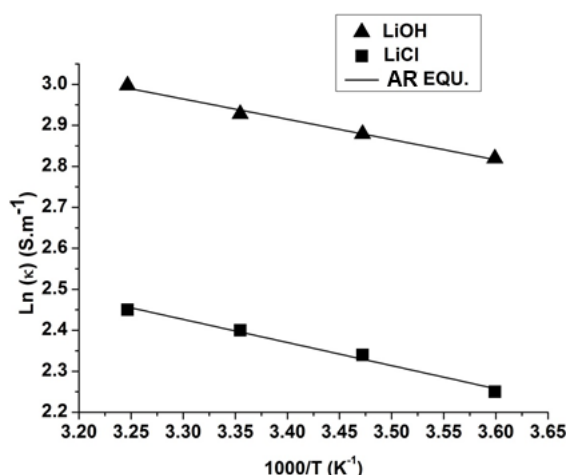
Fig 6. Arrhenius plot of the specific conductance κ of LiOH and LiCl in chitosan

and appears to be influenced by the solution viscosity, as they have been already noticed by Christie et al. when studying conductivities of lithium salt complexes in propylene carbonate [16].

Ionic conductivity data (κ) for LiCl and LiOH in chitosan, using the concentration 0.1 mol dm^{-3} and in the temperature range 278–308 K are presented in Table 4 and represented in Fig. 5. We can see that the conductivity increases when the temperature increases because the viscosity of the electrolyte is reduced. In Fig. 6, we plot the natural logarithm of κ versus 1/T K.

The maximum electrical conductivity (κ$_\infty$) was determined by assuming a linear fit of ln (κ) versus 1/T. In our case, κ$_\infty$ of LiOH and LiCl in chitosan were equal to 98.5 S m^{-1} and 72.24 S m^{-1}, respectively. Then, the activation energy (E$_a$ = 4.22 meV for LiOH and E$_a$ = 4.83 meV for LiCl) was evaluated from the slope (B = E$_a$/kB). It is noticeable that these results were also previously found by other researchers [17].

■ CONCLUSION

The purpose of the present study was to test simple models for the conductivity of biodegradable electrolyte used in a clean battery. The variations of the molar conductivity with salt concentration followed Fuoss's ion paired model. The electrical conductivities of above-mentioned systems have been determined to fit the empirical Gasteel–Amis equation. It was found that the values of (b) were all negative. The study presented in this paper proved that Arrhenius equation can also be used to describe the temperature dependence of the electrical conductivities. The activation energy of the electrolyte was obtained by the linear fit of ln (κ) versus 1/T. In view of these results, the electrolyte based on chitosan has been optimized and can be used in clean batteries.

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