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Classification of Glassy and Polymer Electrolytes for Lithium-ion Batteries by the Bond-Strength-Coordination Number Fluctuation Model

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Abstract. This article deals with the classification of glassy and polymer electrolytes for lithium-ion batteries into the so-called “strong/fragile” scale, by the means of the bond-strength-coordination number fluctuation model. We have evaluated the strength parameter, which plays a key role in the understanding of the relaxation phenomena, of each lithium-ion conductor under consideration. We have derived a relationship that not only describes accurately the experimental results, but also provides important details on the interrelation between the strength parameter, the bond strength of the structural unit, the binding energy, the coordination number and the glass transition temperature.

Introduction
In order to cope with the problem of conversion efficiency and gaseous exhaust, recently, lithium-ion conducting glasses, polymers and ceramics have attracted considerable interest due to their technological importance for a variety of devices such as batteries, hybrid power sources, fuel cells, supercapacitors, sensors, gate membranes for controlled release of anionic drugs, electrochemically switchable ion-exchangers for water purification, etc. [1]. Among these potential applications, lithium-ion batteries are of outmost importance. The potential of these unique power sources make it possible to foresee an even greater expansion of their area of applications to technologies that span from medicine to robotics and space. However, battery performance depends critically on the materials used.

In the present study, we have evaluated, by the means of the bond-strength-coordination number fluctuation model, the strength parameters of a series of lithium-ion conducting glasses and polymers. Such evaluation enabled us not only to classify the glassy and polymer electrolytes into the so-called “strong/fragile” scale, but also helped us to provide insightful details on the relationship between the strength parameter, the bond strength of the structural unit, the binding energy, the coordination number and the glass transition temperature.

An Overview on the Bond-Strength-Coordination Number Fluctuation Model
Recently, we have carried out many studies based on the bond-strength-coordination number fluctuation (BSCNF) model [2]. For instance, this model enabled us to correlate the temperature range of cooperativity and the fragility index in polymeric materials [3,4], and to confirm the existence of a correlation between α and β-relaxations in glass-forming liquids [5]. Let us mention that the BSCNF model incorporates the well-known Vogel-Fulcher-Tammann (VFT) law [6].

In the framework of the BSCNF model, the melt is considered as an agglomeration of structural units and the viscous flow occurs when they move from one position to another by breaking the bonds connecting them. Each structural unit is bound to other structural units by a certain bond strength. The viscosity of the melt increases if the temperature of the system is lowered, due to the increase in the connectivity between structural units. The spatial distribution of structural units is frozen at the glass transition temperature.
According to this model, the temperature dependence of the viscosity is written as [2]

\[
\ln(\eta / \eta_0) = \frac{C_x + Cx^2\left(\ln(\eta_{Tg} / \eta_0) + \frac{1}{2} \ln(1-B) \frac{(1-B)}{C} - 1\right)}{1-Bx^2} - \frac{1}{2} \ln(1-Bx^2),
\]

where \( C = \frac{E_0 Z_0}{RT_g} \), \( B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2} \) and \( x = T_g / T \).

\( \eta_0 \) and \( \eta_{Tg} \) denote the viscosity at high temperature limit and at glass transition temperature \( T_g \), respectively. \( C \) contains information about the total bond strength of the structural unit and \( B \) gives its fluctuation. \( E_0 \) is the average value of the binding energy between the structural units and \( Z_0 \) is the average value of the coordination number of the structural units. \( \Delta E \) and \( \Delta Z \) are the fluctuations of \( E \) and \( Z \), respectively. \( R \) is the gas constant.

**Evaluation of the Ideal Glass Transition Temperature**

The bond-strength-coordination number fluctuation model discussed in the preceding section led us recently [3-6] to propose the following equation for evaluation of the ideal glass transition temperature \( T_0 \)

\[
T_0 = T_g \left[ 1 - \frac{1}{m \ln(10)} \left( 1 + \sqrt{B^*} \left( \frac{C^* - 1}{2} \ln(1-B^*) \right) \right) \right],
\]

where \( m \) represents the fragility index. The characteristic parameters \( B^* \) and \( C^* \) denote respectively the values of \( B \) and \( C \) that obey the following equation

\[
C^* = \frac{2\gamma(1-B^*)}{2\gamma + \sqrt{B^*(1+\gamma^2)}} \left( \ln(\eta_{Tg} / \eta_0) + \frac{1}{2} \ln(1-B^*) \right), \quad \text{with} \quad \gamma = \frac{|\Delta E|}{E_0 |\Delta Z| / Z_0} = 1.
\]

It is well established that the fragility index can be expressed as follows [7]

\[
m = \lim_{T \to T_g} \frac{d \log \eta}{d (T_g / T)}.
\]

According to the BSCNF model, the relationship between the fragility index and the parameters \( B^* \) and \( C^* \) is given by [2]

\[
m_{B^*C^*} = \frac{1}{\ln(10)} \left( B^* - C^* + 2 \left( \ln \left( \frac{\eta_{Tg}}{\eta_0} \right) + \frac{1}{2} \ln(1-B^*) \right) \right).}
\]

On the other hand, so far, it has been widely accepted that the whole pattern of thermal behavior of viscosity of glass-forming liquids can be described by the following VFT equation

\[
\eta = \eta_0 \exp \left( \frac{D_T}{T - T_0} \right),
\]

where \( m_{B^*C^*} \), \( B^* \) and \( C^* \) are the characteristic parameters.
where $D$, which is usually expressed in terms of the constant $B_{VFT} = DT_0$, refers to the strength parameter quantifying the divergence from Arrhenius temperature dependence. Higher $D$ leads to more Arrhenius-like behavior. The ideal glass transition temperature can be extracted from Eq. 7 as

$$T_0 = T_g \left[ 1 + \frac{D}{\ln(10) \log(\eta_{Tg}/\eta_0)} \right]^{-1}. \quad (8)$$

The fragility index $m_{VFT}$ can be derived from Eqs. 5 and 7 as

$$m_{VFT} = \frac{1}{\ln(10)} \left[ \frac{DT_0}{T_g^2} \left( \frac{T_0}{T_g} \right)^2 \right]. \quad (9)$$

**Evaluation of the Strength Parameters: Classification of Glassy and Polymer Electrolytes**

By using Eqs. 3 and 8, we can deduce the following expression of the strength parameter which provides important details on its relationship with the bond strength of the structural unit, the binding energy, the coordination number and the glass transition temperature (via the parameters $B^*$ and $C^*$)

$$D = \ln(10) \log(\eta_{Tg}/\eta_0) \left[ \frac{\left( 1 + \sqrt{B^*} \right) C^* - \frac{1}{2} \ln(1 - B^*)}{m \ln(10) - \left[ \frac{1 + \sqrt{B^*}}{1 - B^*} \right] C^* - \frac{1}{2} \ln(1 - B^*)} \right]. \quad (10)$$

Recently [8], Nascimento et al. have fitted the VFT equation with reliable experimental data of various glasses near $T_g$ to $T_m$ (melting temperature). Similar work has been conducted by Klein et al. [9] on many plasticized and neat lithium-ion conducting polymers. By using the VFT parameters obtained by these two groups, we have calculated, on the one hand, the exact values of the ratio $\eta_{Tg}/\eta_0$ for each material sample, thanks to Eq. 7 (at $T_g$). On the other hand, such parameters enabled us to calculate the values of the corresponding fragility indexes. However it must be emphasized that we have observed a discrepancy between the values of the fragility index obtained here (from VFT law) and those reported in Ref. 8. Such situation results from the fact that Nascimento et al. have considered the ratio $\eta_{Tg}/\eta_0$ as constant ($\sim 10^{17}$), which is not the case for the materials in consideration here.

In Fig. 1 we have displayed the behavior of Eq. 10. The exact values of $B^*$ and $C^*$ have been calculated thanks to Eqs. 4 and 6. As it can be observed, the strength parameter decreases when the material becomes more fragile. It is gratifying to note that the values of $D$ obtained here coincide exactly with those reported in Ref. 8, for lithium-ion conducting glasses, and in Ref. 9, for lithium-ion conducting polymers. As shown in the inset of Fig. 1, for each group of material, we have made a classification into the so-called “strong/fragile” scale. From top to bottom, the materials become more fragile.
An analysis of Fig. 1 indicates that the lithium-ion conducting glasses considered here are stronger, with some exceptions however, than the lithium-ion conducting polymers. For the former case, there is an apparent increase in the strength parameter with the increase of silicate or borate content. As aforementioned, Eq. 10 highlights the relationship between the strength parameter, the bond strength of the structural unit, the binding energy, the coordination number and the glass transition temperature. In our knowledge, such a relationship is new and has not been published yet.

Summary

An important achievement of the work presented in this paper is the relationship derived from the bond-strength-coordination number fluctuation model that links the key features of relaxation phenomena in glass-forming liquids, i.e. the strength parameter, the bond strength of the structural unit, the binding energy, the coordination number and the glass transition temperature. Having investigated the behavior of the strength parameter with the variation of the fragility index in various lithium-ion conductors, we may conclude that glassy and polymer electrolytes for lithium-ion batteries can be well classified into the so-called “strong/fragile” scale.

References