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TRANSPORT PROPERTIES OF BINARY SALT POLYMER ELECTROLYTES

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Abstract

Transport properties (ionic conductivities (σ), salt diffusion coefficients (D_s), and cationic transference numbers (t_+^0)) as a function of salt concentration (C_s) are reported and compared for several common binary salt/polymer systems being considered for use as electrolytes in rechargeable lithium batteries for electric vehicle and other applications. The three properties provide a complete description of transport in solid polymer electrolytes (SPEs) or "dry" systems in cells undergoing galvanostatic charge and discharge. The macroscopic approach used obviates the need to know the details of speciation in these non-ideal solutions and allows for a more sophisticated correlation of the characteristics of ion transport with polymer structure, salt type, and concentration than conductivity data alone.

Introduction

Rechargeable metallic lithium batteries need highly conductive and minimally reactive electrolyte solutions to ensure the safe operation and long cycle life required for electric vehicle applications. The high reactivity with lithium and flammability of most organic liquids preclude their use in secondary batteries with metallic lithium anodes; thus, the safest choices, at present, are solid polymer electrolytes (SPEs) rather than gels or liquid-based systems. SPEs typically consist of a polymer host (most commonly based on poly(ethylene oxide) or another polyether) complexed with a low lattice energy lithium salt. Because these binary salt/polymer solutions are commonly used above their melting points, they are perhaps more accurately classified as non-Newtonian liquids rather than true solids. Their safety features are related to their high viscosity, and ability to form a solid electrolyte interface layer in the presence of lithium, preventing further reaction and effectively sealing off the lithium surface from air and water in the case of a breach. There is also evidence that the use of SPEs suppresses dendrite formation in well-designed systems. [1] The dimensional stability also has design advantages for fabrication of series stacks; configurations that are necessary for large-scale applications such as electric vehicles. Unfortunately, the ionic conductivity of SPEs is usually one or more orders of magnitude lower than that of gels or liquid electrolytes (typically $\sim 10^{-3}$ S/cm) at the cell operating temperature; to compensate for this, very thin (<100 μm) components are used.

Conductivity alone is not sufficient to describe the behavior of electrolyte solutions in which both cations and anions are mobile. According to concentrated solution theory, for three-component (cation, anion, solvent) systems, two additional properties are needed; e.g., salt diffusion coefficient (D_s) and cationic transference number (t_+^0). Unfortunately, there has been much confusion about the measurement and interpretation of t_+^0 in polymer electrolytes. This is due, in part, to inaccurate simplifying assumptions about the ideality of the solutions, as well as to experimental difficulties. We have recently developed an electrochemical Hittorf method based on concentrated solution theory for determination of transport properties, including t_+^0 , for binary

salt/polymer electrolytes.[2, 3]. No assumptions are made concerning the ideality of the solutions, and the method is based on a macroscopic interpretation of ion transport phenomena; i.e., no details about the nature of speciation in the solutions are required. Instead, t_+^0 is obtained as a function of salt concentration from the combined results of three different electrochemical measurements; concentration cells, current interrupt, and restricted diffusion data for each composition. Although this requires a fair amount of experimentation, a complete description of each system is obtained, allowing accurate modeling of the polymer electrolyte behavior in cells undergoing discharge. [2] To date, this information, in particular t_+^0 as a function of salt concentration, has not been available, and the nature of ion transport in SPEs in cells undergoing galvanostatic charge and discharge has been poorly understood. Detailed information about the transport properties of various polymer electrolyte systems as a function of salt concentration and other properties also allows a more sophisticated comparison than conductivity data alone, and may have predictive value. It is the purpose of this paper to gather together information we have obtained in this laboratory for the purposes of determining how polymer structure, salt concentration and type, and other properties affect ion transport in SPEs.

Experimental

Conductive, dimensionally stable, binary salt/polymer systems with high conductivity and low reactivity towards electrode materials were selected for study. Systems investigated to date include high molecular weight polyethylene oxide (PEO $M_n = 5 \times 10^6$, Aldrich Chemical Company), polypropylene oxide (ParelTM, PPO, $M_n = 2.5 \times 10^5$, Zeon Chemicals, Inc., Illinois, USA) or oxymethylene-linked polyethylene oxide ("amorphous PEO" or PEMO, $M_w = 1 \times 10^5$) complexed with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI), $\text{NaN}(\text{CF}_3\text{SO}_2)_2$ (NaTFSI), LiCF_3SO_3 (LiTf) or NaCF_3SO_3 (NaTf). Colorless, sticky and flow-resistant PEMO was produced using a Williamson ether synthesis technique. [4] Purification was accomplished by: (1) vacuum filtration of the reaction products from a methylene chloride solution, (2) water/methylene chloride 3x wash in a separatory funnel, (3) multiple precipitation from methylene chloride by slow addition of heptane (4) drying at 80° C in-vacuo over P_2O_5 . The average molecular weight was determined using gel permeation chromatography (DMF solvent, Rainin HPXL, Knauer Differential Refractometer and a Plgel 10 μm Minimix-B column). Monodisperse polystyrene standards were used for calibration of the GPC experiment. Prior to fabrication of films, commercial polymers and salts were purified to remove water, additives, and stabilizers by Soxhlet extraction and/or recrystallization as described in [5]. Materials were then dried extensively over P_2O_5 in a drying pistol and stored in an inert atmosphere glove-box prior to use. Solutions of polymer and salt in dimethoxyethane or acetonitrile were prepared in the glove-box and cast onto Teflon-coated glass, to form films ~50-100 μm thick after drying in an inert atmosphere. Films were never exposed to air, and were not heated above room temperature prior to study.

Differential scanning calorimetry (Perkin-Elmer DSC-7) was used to determine the phase behavior of the films, for a wide range of salt concentrations. Films were encapsulated in aluminum capsules under inert atmosphere prior to transfer to the DSC

instrument. Glass transition temperatures (T_g) and melting points (T_m) were determined during the second heating cycle at 5-10° C/minute under inert atmosphere to ensure that the thermal histories of the samples were well-controlled. An exception was made for the PEO-LiTFSI electrolytes for which T_g and T_m was obtained during the first heating cycle due to the extremely slow recrystallization process of this system. [6] AC impedance measurements as a function of temperature were also employed to confirm melting transitions, using a Solartron SI 1254 four-channel frequency response analyzer. Best results for transport property measurements are obtained in salt concentration and temperature ranges in which samples are single-phase and have high conductivity. Another important criterion is the relevance to operating cells. Most SPEs are used at somewhat elevated temperatures (>60° C). Unless otherwise noted, a temperature of 85° C was selected for the systems described herein.

Salt diffusion coefficients (D_s) of single-phase binary salt/polymer solutions were determined as a function of salt concentration, using a restricted diffusion method. [2,3] Symmetrical cells containing polymer films of known thickness (L) are galvanostatically polarized, for a short time. After the current is turned off, the cell potential ($\Delta\Phi$) relaxes back to 0V; at long times, equation (1) holds true, where A is an intercept value.

$$(1) \ln \Delta\Phi = \frac{\pi^2 D_s}{L^2} t + A$$

These results and those of two other electrochemical experiments are combined to obtain t_+^0 (equation 2) for each salt concentration, and set of conditions. In equation 2, C_∞ refers to the bulk salt concentration, F is Faraday's constant, and the condition $t_+^0 + t_-^0 = 1$ is used.

$$(2) t_-^0 = 1 - t_+^0 = \frac{m C_\infty F (\pi D_s)^{1/2}}{4} \left(\frac{d \ln C}{dU} \right)$$

Data from concentration cells, i.e., symmetrical cells containing two polymer electrolyte films with differing salt concentrations, is required for the last term in equation 2. The salt concentration of the first film is held constant and that of the second (C) is varied. The potential (U) is then determined and plotted against $\ln C$ for the entire range of concentrations. $(d \ln C / dU)$ is then derived from the local slopes at $C=C_s$. The slope, m , in equation 2 is derived from the linear portion of a plot of open circuit potential (OCP) vs. $it^{1/2}$, from galvanostatic polarization/current interrupt experiments on symmetrical cells containing polymer electrolyte films. Current (i) is run for a short time (t) through symmetrical cells containing a polymer electrolyte film, and the OCP is read just after the current is interrupted. The data from several experiments with differing $it^{1/2}$ values are used to generate the plots for each polymer electrolyte composition. The concentration cell data can then be correlated with the concentration gradient induced by the applied current in the polarization/current interrupt experiments. For further experimental details, consult references [2] and [3].

Results and Discussion

The complete transport and thermal properties of PEO/NaTf [2], PEO/NaTFSI [7], PPO/LiTf [5], PPO/LiTFSI [8] and PEO/LiTFSI [6, 9] have been determined at 85° C, and partial data has been obtained on PEO/LiTf and LiTFSI systems at 40°, 60° and 85° C. Figure 1 shows σ vs. C_s data and Figure 2 shows t_+^0 vs. C_s data for the five completed systems at 85° C. At low C_s , the scarcity of charge carriers causes conductivities to be low, whereas at high C_s , increasing viscosity and ion aggregation decrease the conductivity from the maximum observed at moderate concentrations. In contrast, the t_+^0 behavior varies with the system under investigation, but generally decreases with increasing C_s . This reflects the increasing ion aggregation in highly non-ideal polymer electrolyte solutions. The observation of negative t_+^0 s in some cases indicates that negatively charged species, rather than free lithium ions, are the major charge carriers. (Note: negative t_+^0 values are possible because t_+^0 is defined as the net number of moles of the cationic species crossing a reference plane fixed with respect to the solvent, when one Faraday of current is passed.[10] Li^+ ions make a negative contribution to t_+^0 if they are complexed in mobile negatively charged aggregates). While cells undergoing galvanostatic discharge can operate for a time with these polymer electrolytes, negative or non-unity numbers imply that concentration gradients will accumulate, resulting in premature failure due to salt precipitation or depletion in poorly designed systems.[11] Non-unity values of t_+^0 are also seen in liquid electrolyte systems that contain salts with mobile anions; in some cases where negative complexes are found in concentrated solution (e.g., zinc halides in water) t_+^0 is negative. [12] While concentration gradients are also expected to arise in such systems upon cell charge or discharge, they are more easily dispersed due to the higher salt diffusion coefficients in liquids. The mobility of the solvent itself may also play a role in the persistence of concentration gradients; in SPEs, the polymer does not normally undergo translational motion on short time-scales, whereas small organic molecules do. Thus, low values of t_+^0 have more serious consequences for the operation of SPE cells than for those containing liquids.

Unfortunately, the overall ionic conductivity is often lowered in systems with higher t_+^0 values (e.g., PPO), reflecting the fact that negatively charged ionic aggregates are relatively immobilized by the host matrix rather than that transport of cations is improved. Similarly, t_+^0 values are generally lower for polymer solutions with sodium salts than with the analogous lithium ones (compare PEO/NaTFSI and PEO/LiTFSI), although conductivities are similar. Systems with TFSI-containing salts generally exhibit higher and less concentration-dependent t_+^0 values than those with Tf anions, but conductivity is not compromised. This is particularly evident in electrolytes containing LiTFSI, in which positive, relatively C_s -invariant t_+^0 values are found regardless of polymer type (PPO, PEO, PEO). LiTFSI has a low lattice energy, which promotes

dissociation in host polymers with low dielectric constants. The TFSI anion and anionic complexes have less mobility than smaller anions, especially at high C_s where free volume is lowered; thus t_+^0 does not decrease as considerably with C_s as in other polymer/salt systems. The insensitivity of t_+^0 to C_s is an advantage in systems containing LiTFSI because the transport properties do not become less favorable as concentration gradients develop in cells undergoing galvanostatic discharge. In contrast, D_s and t_+^0 both decrease markedly as C_s increases in PEO/NaTf causing a "snowball" effect. Salt precipitation results in premature failure of operating cells with polymer electrolytes having a high initial C_s . Interestingly, it is possible to double the rate capability of sodium/polymer/manganese oxide cells simply by decreasing the initial salt concentration of the PEO electrolyte. [11] Exaggerated capacity fading upon cycling is seen in cells in which salt precipitation has occurred; most likely because complete re-dissolution does not take place even after long rests, and the presence of nucleation sites causes precipitation to occur earlier in subsequent discharges. Thus, transport properties may affect not only rate capability (or, alternatively, limit the thickness of components) but also cycle life, especially in cases where t_+^0 is very low or negative.

These results show that salt concentration and type, as well as the nature of polymer host affect transport properties in complex ways. Operating temperature also influences transport properties; most notably, conductivity decreases markedly as temperature is lowered. In crystalline or partially crystalline systems such as those based on PEO, conductivity below the melting point is usually insufficient to allow cell operation, except at very low current densities. PEMO ("amorphous" PEO) is an oxymethylene-linked poly(ethylene glycol); the interruption of the ethylene oxide units by CH_2O inhibits crystallization of the salt complexes, resulting in low melting points. As a result, conductivities are relatively high at 25° C (as high as 10^{-4} S/cm), allowing cell operation at ambient temperatures, albeit at low current densities. [13]

The amorphous nature and high conductivity of PEMO/salt complexes allows flexibility in the choice of operating temperature, unlike in PEO or PPO systems. At elevated temperatures, both σ and D_s can be expected to increase but t_+^0 behavior is less easy to predict because of the complexity of ion aggregation reactions, which are strongly influenced by temperature. In PEMO systems, it appears that t_+^0 increases with increasing temperature for both LiTf and LiTFSI salt solutions (Table 1). This may reflect a relative increase in the mobility of free Li^+ ions upon heating, since ion aggregation tends to increase with temperature in many polymer systems. While conductivities near room temperature are sufficient to allow operation of cells, the t_+^0 data indicate that better performance is expected at elevated temperatures because concentration polarization will be slower to develop. Both the transport and physical properties of the salt/polymer complexes need to be considered, however, when selecting the operating temperature of cells with PEMO-based electrolytes, which tend to soften considerably upon heating.

These results suggest that there is often a trade-off between overall conductivity and t_+^0 in binary salt/polymer systems that conduct by a free-volume mechanism, because negatively charged species are intrinsically more mobile than free cations or positive

aggregates. In general, Li^+ is transported by negatively charged ionic aggregates in concentrated solutions, and decreasing their concentration or mobility adversely affects conductivity. Design of single-ion polymeric conductors with immobilized anions may be severely limited by this feature. Salts with low lattice energies and large anions ameliorate this tendency because of increased dissociation of ions, and a larger free volume at high C_s . A more fruitful approach may be to design new salts and polymers in which these features are enhanced. This will require complete understanding of how polymer and salt type and structure affect ion transport.

Near-term research should be directed towards development of novel low lattice energy salts and polymers that promote Li^+ mobility without unduly compromising conductivity. Other promising approaches involve use of composite electrolytes (e.g., a high-conductivity gel sandwiched between two thin single-ion conducting layers) or gelled polymer systems containing minimal solvent. Research with a longer term outlook should be directed towards finding polymer systems in which the ionic conduction mechanism is not associated with polymer segmental motion.

Conclusions

The electrochemical method developed in this laboratory for the determination of transport properties of binary salt/polymer solutions has been applied to a number of SPEs. This method has the advantages of theoretical rigor and experimental ease, and allows a great deal of information to be obtained fairly rapidly. The information can then be used to predict behavior of cells passing current accurately. The results described herein show that polymer host, salt type and concentration, as well as temperature influence t_+^0 in complex and sometimes surprising ways. Knowledge of all the transport properties allows a more sophisticated approach to the design of polymer electrolytes and devices based upon them than just that of conductivity alone. We intend to expand the scope of our studies to include various salts and co-polymers as well as comb-branched systems to improve understanding of how polymer architecture and anion type influence transport.

Acknowledgments

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Figure Captions

Figure 1. Conductivities at 85° C as a function of salt concentration for the PEO/NaTFSI (×), PEO/NaTf (◇), PPO/LiTf (●), PPO/LiTFSI (■) and PEO/LiTFSI (□) polymer electrolyte systems.

Figure 2. t_+^0 values at 85° C as a function of salt concentration for the PEO/NaTFSI (×), PEO/NaTf (◇), PPO/LiTf (●), PPO/LiTFSI (■) and PEO/LiTFSI (□) polymer electrolyte systems.

Table 1**Transport Properties of PEMO/salt solutions**

PEMO/LiTFSI				
C_s, M/L	EO:Li	Temperature, °C	σ, S/cm	t₊⁰
1.08	20	40	2.8x10 ⁻⁵	0.14
1.08	20	60	2.1x10 ⁻⁴	0.33
1.08	20	85	5.2x10 ⁻⁴	0.49
1.3	15	40	1.2x10 ⁻⁴	0.14
1.3	15	60	3.6x10 ⁻⁴	0.35
1.3	15	85	1.1x10 ⁻³	0.48
2.06	8	40	6.3x10 ⁻⁵	-0.15
2.06	8	60	1.5x10 ⁻⁴	0.22
2.06	8	85	7.4x10 ⁻⁴	0.38
PEMO/LiTf				
1.25	20	40	3x10 ⁻⁵	-0.14
1.25	20	60	9x10 ⁻⁵	0.05
1.25	20	85	2.5x10 ⁻⁴	0.31

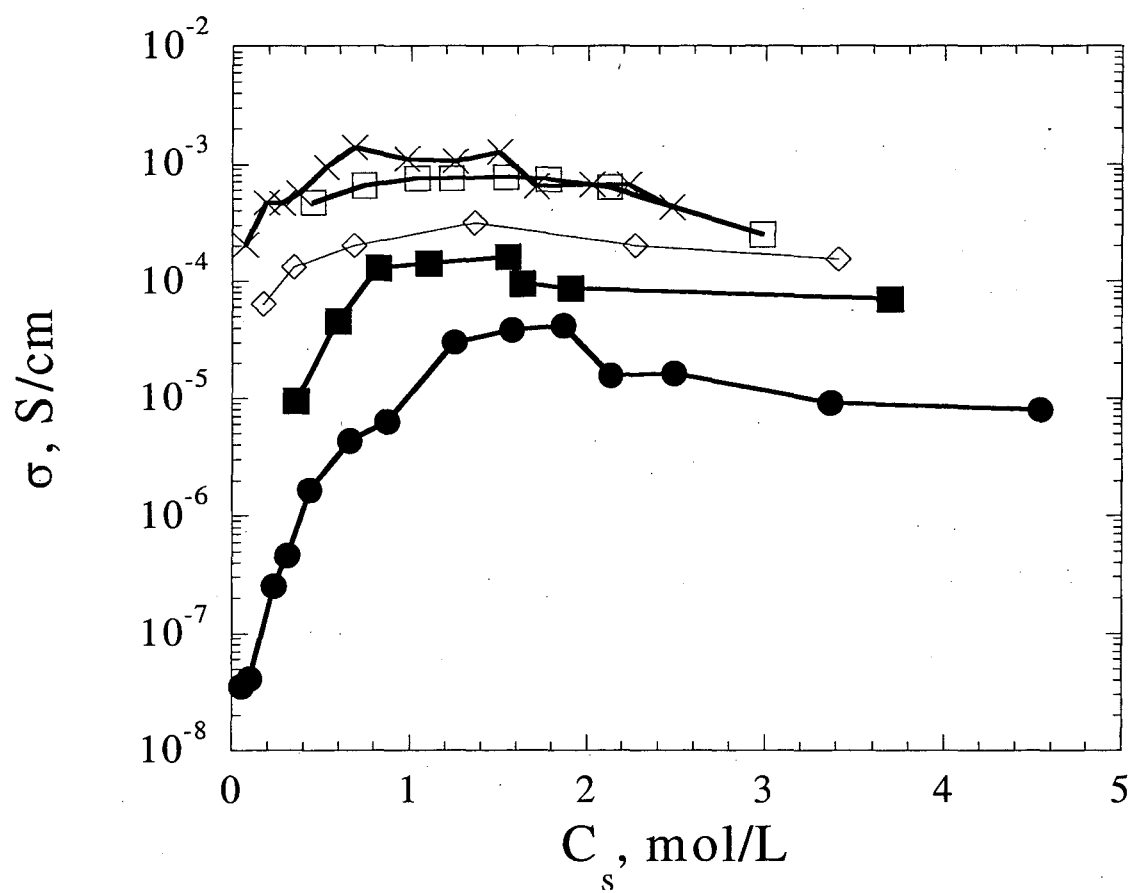


Figure 1

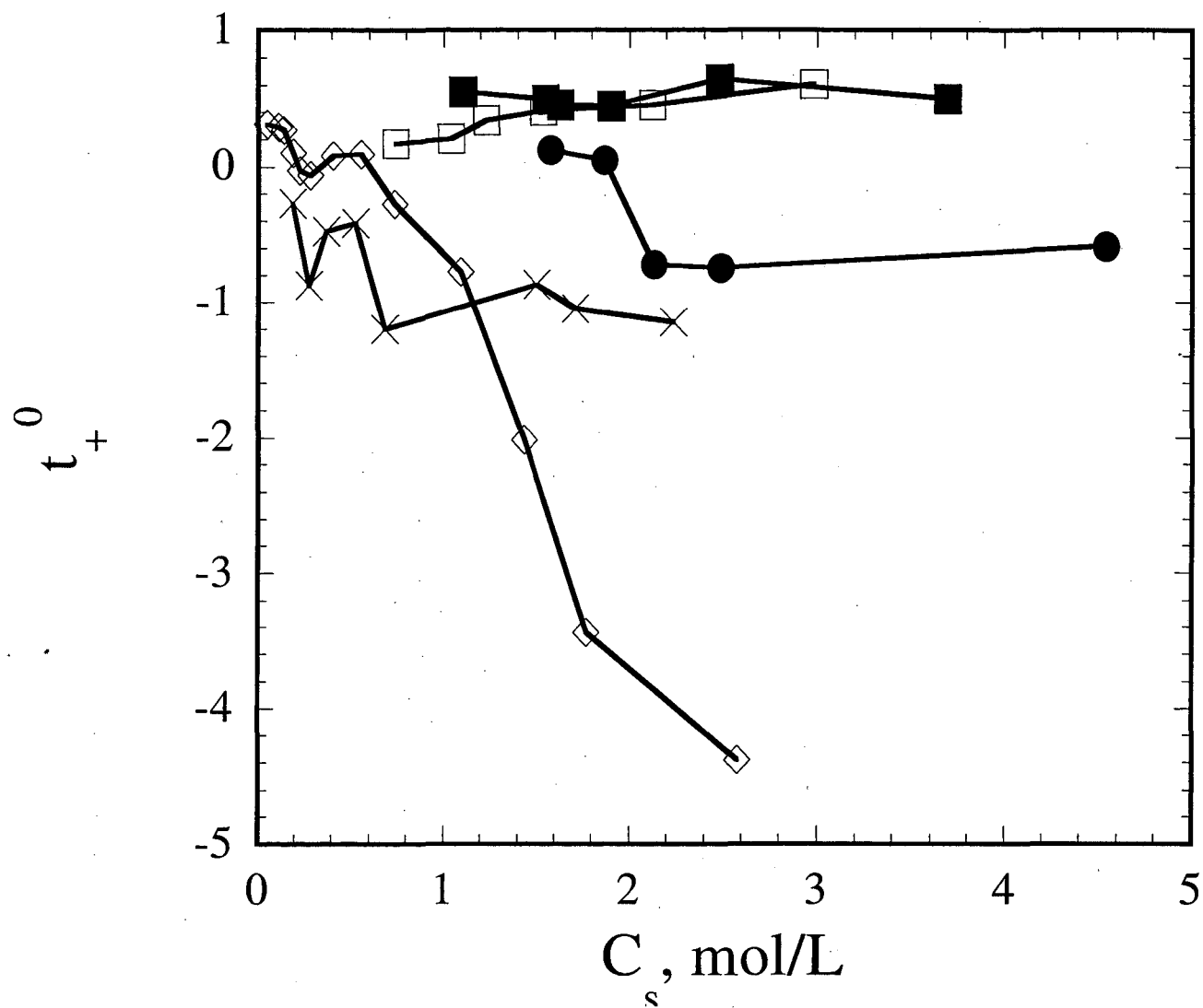


Figure 2

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