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Theoretical Simulation of Solid Polymer Electrolytes Based on Poly(vinylidene fluoride) with Lithium Salts for Lithium-Ion Battery Application

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Abstract. Solid polymer electrolyte composited by poly(vinylidene fluoride) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) has been optimized for solid-state lithium-ion batteries taking into account the LiTFSI concentration. Computer simulations of battery systems was used to evaluate the influence of LiTFSI concentration at different battery operation temperatures (278.15 K, and 353.15 K) and different discharge rates (C/30 and 3C), evaluating also the dissipated ohmic heat. It is shown how battery performance depends on LiTFSI content, which is correlated with ionic mobility, diffusion and temperature. A minimum of 30% of LiTFSI content is essential to obtain suitable solid polymer electrolytes for battery operation.

Keywords: Solid polymer electrolyte, delivery, simulation, solid-state lithium-ion battery.

INTRODUCTION

There is an increasing demand for energy resources considering the population growth and economic development. At the same time, to reduce the environmental impact of fossil fuels, an energy transition to cleaner energy sources is taking place [1].

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One of the biggest problems of cleaner renewable energy sources such as wind and solar, is their intermittent supply, being therefore needed their coupling with energy storage systems [2].

Lithium-ion batteries are one of the most used types of energy storage systems, which are experiencing a significant growth due to their use in electric vehicles, in the scope of reducing CO_2 emissions. Nevertheless, conventional lithium-ion batteries need to improve their safety and environmental impact since the commonly used electrolyte solution is toxic and dangerous. To solve this problem, the separator and electrolyte solution are aimed to be replaced by solid polymer electrolyte (SPE) [3].

SPEs consist of a polymer matrix and different fillers in which the matrix guarantees mechanical/thermal stability and fillers are responsible for the ionic conductivity, having no liquid components [4].

The ionic conductivity value of current SPE is still not sufficient ($< 10^{-5}$ S/cm at room temperature) for their use in solid-state lithium-ion batteries, the scientific works in this area being mainly devoted to improve the value of the ionic conductivity and to understand tailor its behavior [5].

The present study focuses on the computer simulation of a SPE composed by poly(vinylidene fluoride) (PVDF) as a polymer matrix doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in half-cathodic cells as a function of LiTFSI concentration, cycled at different scan rates. The thermal behavior of these cells was also obtained, the SPE thickness being kept constant.

METHODOLOGY

The delivered capacity value and the heat produced in the SPE when the LiTFSI concentration increases from 10% to 60% is evaluated (Figure 1). The theoretical simulation was conducted based on the electrochemical model that governs the battery operation for SPE and cathode through the Finite Element Method.

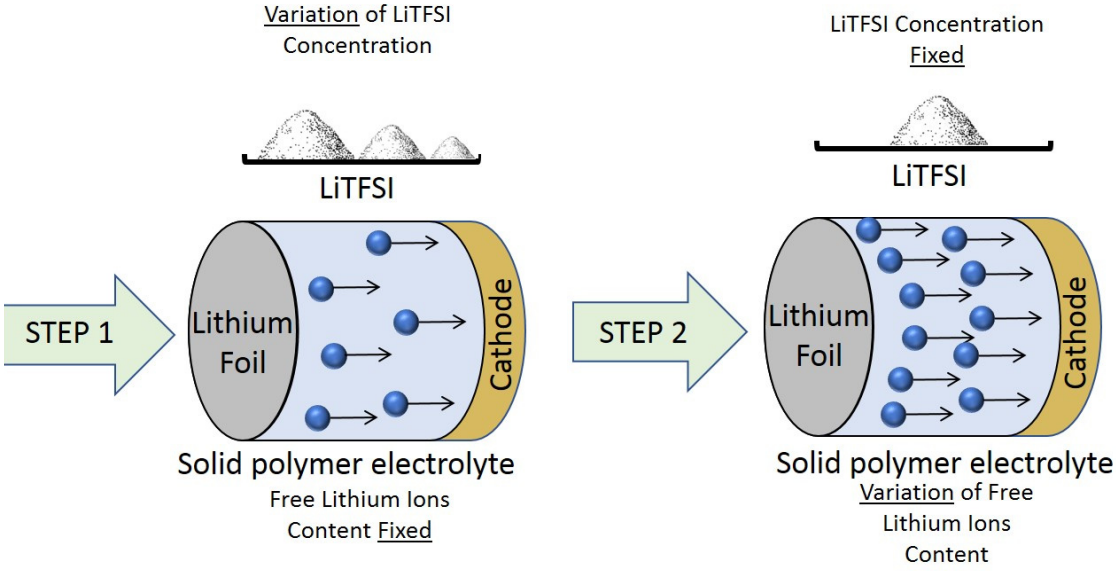

FIGURE 1. Schematic illustration of the half-cathodic cells as a function of LiTFSI concentration applied to simulated batteries.

Table 1 shows the different parameter values introduced in the simulations of the SPE and the cathode in Li/Li_xFePO_4 half-cells. The mathematical equations of these simulations can be consulted in [6].

TABLE 1. Parameters and initial values introduced in the theoretical simulations applied to electrodes and SPE.

Electrochemical, thermal and general parameters and initial values

Parameter	Unit	Solid polymer electrolyte	Cathode (Li_xFePO_4)
Width of the battery component (*L*)	m	100×10^{-6}	77×10^{-6}
Initial concentration of lithium-ions (c_{0,Li^+})	$mol.m^{-3}$	3483.23 [d] × δ	
Free lithium ions fraction in equilibrium (δ)	-	[0.10,0.50]	
Maximum lithium concentration in the cathode ($c_{Li,max}$)	$mol.m^{-3}$		23300
Minimum lithium concentration in the cathode ($c_{Li,min}$)	$mol.m^{-3}$		10200
Recombination reaction rate (k_{rec})	$m^3.(mol.s)^{-1}$	0.9×10^{-8} [a]	
Diffusion coefficient for lithium ions at 298,15K ($D_{Li^+,298.15K}$)	$m^2.s^{-1}$	0.8×10^{-11}	
Diffusion coefficient for negative ions at 298,15K($D_{n^-,298.15K}$)	$m^2.s^{-1}$	1.0×10^{-11}	
Diffusion coefficient of solid lithium at the positive electrode (D_{Li})	$m^2.s^{-1}$		1.8×10^{-15}
Charge transfer coefficient at positive electrode (α_c)	-		0.6 [a]
Charge transfer reaction rate constant at positive electrode (k_c)	$mol.(m^2.s)^{-1}$		5.1×10^{-4} [a]
Activation energy for diffusion of lithium ions (E_{a,Li^+})	$J.mol^{-1}$	101×10^3	
Activation energy for diffusion of negative ions (E_{a,n^-})	$J.mol^{-1}$	107×10^3	
Activation energy for diffusion in the cathode ($E_{a,c}$)	$J.mol^{-1}$		39×10^3 [b]
Thermal conductivity of the polymer at the solid polymer electrolyte (λ_{poly})	$W.(m.K)^{-1}$	0.20	
Thermal conductivity of the lithium salt in the solid polymer electrolyte (λ_{LiFTSI})	$W.(m.K)^{-1}$	0.85	
Thermal conductivity of the cathode (λ_c)	$W.(m.K)^{-1}$		1.48[c]
Heat capacity of the polymer in the solid polymer electrolyte at constant pressure ($C_{p,poly}$)	$J.(kg.K)^{-1}$	2076	
Heat capacity of lithium salt in the solid polymer electrolyte at constant pressure ($C_{P,LiFTSI}$)	$J.(kg.K)^{-1}$	543	
Heat capacity of cathode at constant pressure ($C_{P,c}$)	$J.(kg.K)^{-1}$		1260.2[c]
Solid polymer electrolyte density (ρ_{poly})	$kg.m^{-3}$	995	
Lithium salt in the solid polymer electrolyte density (ρ_{LiTFSI})	$kg.m^{-3}$	1330	
Cathode density (ρ_c)	$kg.m^{-3}$		1500
Negative electrode (lithium foil)			
Charge transfer coefficient at negative electrode (α_{neg})	-	0.5 [a]	
Charge transfer reaction rate constant at negative electrode (k_{neg})	$mol.(m^2.s)^{-1}$	1×10^{-2} [a]	
General parameters of the battery			
Applied current density at 1C (i_{app})	$A.m^{-2}$	6.10 [d]	
Percentage of solid lithium concentration (*b*)	-	[10%,60%]	
Faraday's constant (*F*)	C.mol-1	96487	
Ideal Gas constant (*R*)	$J.(mol.K)^{-1}$	8.3140	
Temperature (*T*)	K	278.15, 283.15, 298.15, 313.15, 333.15 and 353.15	

a) Based on [7], b) based on [8], c) based on [9], d) experimental value.

RESULTS AND DISCUSSION

The SPE battery performance in the discharge process was evaluated for varying LiTFSI concentration between 10% and 60%, under different thermal conditions including low temperatures (278.15 K and 283.15 K), ambient temperature (298.1 K) and high temperature (353.15 K). Battery discharge rates of C/30, C/20, C/10, C/5, 1C, 2C and 3C were studied, as shown in Figure 2.

In Figures 2a) and 2b), the batteries were subjected to cold environments at temperatures of 278.15K and 283.15 K, respectively. It is observed that the battery capacity values remain constant during the discharge process in the batteries with different LiTFSI content at the low discharge rate of C/30, since the battery requires reduced mobility and lithium-ions diffusion as they travel along the separator during the discharge process. At low temperatures of 278.15 K and 283.15 K and with increasing discharge rate above C/20 and C/10, respectively, batteries with LiTFSI percentages below 30% have significant losses in battery capacity values. At both temperatures of 278.15 K and 283.15 K, there is a drop between 80% and 90% in the discharge capacity with a decrease of LiTFSI concentration from 30% to 10%, at C/10 rate. According to the Arrhenius law applied to the lithium-ions diffusion in the SPE, low temperatures promote low lithium-ions diffusion during the discharge process, that do not correspond to the SPE

lithium-ion mobility and diffusion requirements when subjected to higher discharge rates. This effect is compensated by increasing the amount of lithium-ions in the SPE by increasing LiTFSI concentration. Above 30% LiTFSI concentration, the discharge capacity remains stable regardless of the C-rate.

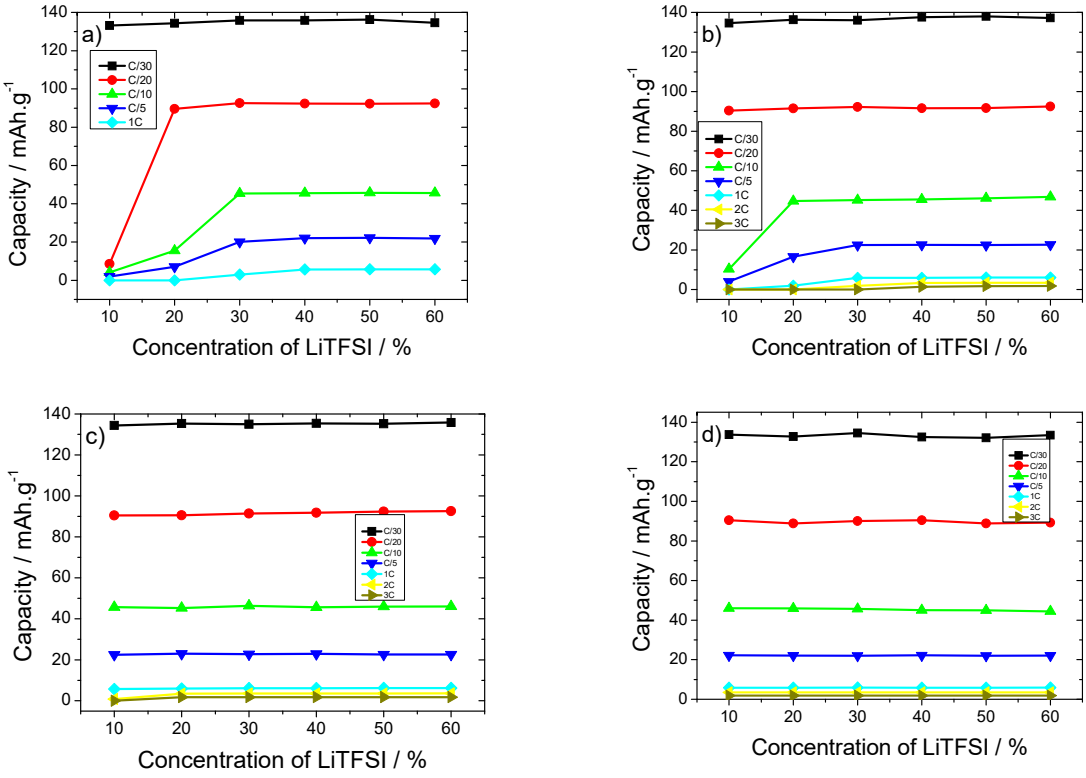

FIGURE 2. Discharge capacity as a function of LiTFSI concentration for scans between C/30 and 3C rates for: a) T= 278.15 K, b) T= 283.15 K, c) T= 298.15 K and d) T= 353.15 K.

It is observed that the different batteries with different LiTFSI concentrations when subjected to ambient temperature of 298.15 K (Figure 2c) and high temperature of 353.15 K (Figure 2d) at different discharge rates (C/30 to 3C), lead to constant values of the discharge capacity, without the occurrence of significant losses in the batteries performance. With the increase of temperature, the diffusion value of lithium-ions increases, allowing a high mobility of the ions that is required from batteries when subjected to high discharge rates.

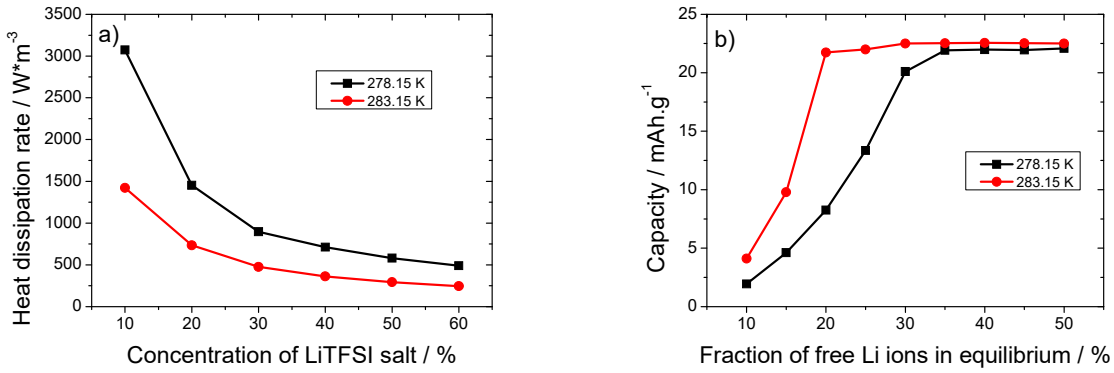

FIGURE 3. a) Heat produced by SPE and b) delivered capacity as a function of free Li ions fraction in equilibrium at C/5 rate and two different temperatures.

For SPE during the discharge process, dissipated heat occurs as shown in Figure 3a). Figure 3a) illustrates the ohmic heat dissipated at various LiTFSI concentrations and temperatures at C/5 rate. Regardless of the temperature, the heat dissipated decreases with increasing LiTFSI concentration due to higher lithium-ion diffusion. Keeping the LiTFSI concentration constant, the heat dissipated decreases when the temperature increases due to the greater diffusion of the ions. Specific battery discharge capacity as a function of charge percentage for the battery with 30% LiTFSI concentration at a discharge rate of C/5 and in cold environments (278.15 K and 283.15 K) are marked by low diffusions, as shown in Figure 3b). At temperatures of 273.15 K and 283.15 K, the capacity values begin to decrease significantly below 30% and 20% LiTFSI concentration, respectively. Thus, a minimum of 30% filler content is be necessary to maintain suitable battery performance at low temperatures, since in cold environments it will be essential to compensate the low diffusion of ions with an increase in the free ions percentage.

CONCLUSION

This work reports on the optimization of a SPE composed by poly(vinylidene fluoride) (PVDF) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) through electrochemical and thermal models. Battery performance depends on LiTFSI concentration and operation temperature. Furthermore, LiTFSI concentration affects ion mobility when subjected to high discharge rates at different temperatures. The dissipated heat is also influenced by the LiTFSI concentration and it is shown that a minimum of 30% LiTFSI content is essential to maintain good battery performance at low temperatures. The understanding of the electrochemical behavior of the SPE is essential to reach the upcoming generation of solid-state lithium-ion batteries.

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