Prediction of Swelling of Polypropylene Separators and its Effect on the Lithium-Ion Battery Performance

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Abstract

The safety and reliability of lithium-ion batteries depend on porous separators, many of which are made of polymer materials, such as polypropylene. Favorable interactions between a separator and organic electrolyte solvents used in the batteries often induce separator swelling. Swelling increases the electric resistance of the cell and is accompanied by plasticization of the separator, which also affects the battery's performance. Here we propose a model based on Flory's theory of polymer solutions which can predict the swelling of a porous polymer separator based on the Flory-Huggins parameter for polymer-solvent interactions. Despite the complexity of the polymer structure, introducing only two additional parameters provides predictive capability for the model. These two parameters can be obtained based on experimental measurements of separator swelling in two different solvents; the model also requires the Flory-Huggins parameter as an input, which can be calculated based on the UNIFAC-FV group contribution method for a given polymer-solvent pair. We illustrated the applicability of this model to recent experimental data on the swelling of polypropylene separators in various solvents. We also showed a simple relation between the separator swelling and an increase in cell resistance. Our model can be used for a quick assessment of various polymer-solvent pairs for application in lithium-ion batteries.

Keywords: Lithium-ion battery; Polymer separator; Porous polypropylene; Polymer swelling; Celgard

Introduction

Currently, the leading solution for electrical energy storage is lithium-ion batteries (LIBs), which provide the highest energy and power per unit mass. Although it is already a well-developed technology, it still has one weak point – safety. A lithium-ion battery failure may cause a thermal runaway, and the battery can catch on fire. A lithium battery cell consists of two electrodes and a separator between them. The role of the separator is to electrically isolate the electrodes but allow ion transport between them; therefore, a separator has to be a thin porous film.[1,2] While the performance characteristics of the batteries (e.g., specific power or specific energy) are determined by the electrode materials, battery safety relies on the separator.

One of the most widely used separators are microporous semicrystalline isotactic polypropylene (iPP) membranes developed almost 50 years ago for alkaline and lead-acid batteries, before the appearance of LIB technology.[3,4] When iPP separators are used with organic solvents utilized in LIBs, the favorable interactions between the iPP and organic solvents result in swelling of the separator.[5,6] Swelling causes a decrease in its porosity and, consequently, an increase in the electric resistance. Furthermore, even insubstantial swelling of the separator is accompanied by its plasticization – a reduction of its mechanical properties. Separator plasticization is harmful for two reasons. First, during regular battery operation, the separator faces compressive loading due to the expansion of electrode particles upon lithium ions intercalation,[7] and a softer separator will be impacted more. Second, the mechanical properties of the separators determine the possibility of a lithium dendrite piercing through it. If a dendrite pierces through the separator, it causes a short circuit and failure of the lithium-ion cell.[8]

Gor et al. performed experiments on a series of solvents and demonstrated that the swelling/plasticization is correlated with the Hildebrand solubility parameters δ for each of the solvents: the most pronounced swelling/softening was observed in the vicinity of $\delta = 17.8\,\mathrm{MPa}^{1/2}$, gradually decreasing for higher and lower δ. They calculated the Flory-

Huggins parameters χ for a polymer with each studied solvent and demonstrated an even better correlation with the observed swelling/plasticization. That work, however, lacked a model which could predict the extent of swelling/plasticization based on the properties of a polymer/solvent pair. The goal of this work is to present such a model for swelling.

Given the complexity of the polymer separators used in Ref. 6, porosity, anisotropy, semicrystalline structure, etc., the development of a rigorous physics-based model would require data on the polymer structure on various scales, which is not available. Therefore, we chose to develop a model which, on the one hand, is based on simple polymer physics but, on the other hand, utilizes some of the polymer properties extracted from the experimental data. Our model uses Flory's model for swelling of a Gaussian chain in solvent,[9] but extends it with an additional parameter related to the polymer microstructure. The model is parameterized based on the data from Ref. 6, and shows good predictive capability so that the experimental measurements of swelling on two solvents are sufficient for predicting swelling in any solvent with known molecular structure. The proposed model allows one to predict the swelling of a porous polymer separator in any solvent knowing the data for two solvents (since the determination of only two parameters is needed). This simplicity secures the practical application of the proposed model. We also showed a simple relation between the separator swelling and an increase in cell resistance.

Models and Methods

The simplest physics-based model for polymer swelling induced by solvents is the model of swelling of a Gaussian chain, proposed by Flory,[9,10] which can be described by the following equation:

$$\alpha^5 - \alpha^3 = C_1 \left(1 - 2\chi\right) Z^{1/2} \tag{1}$$

Where α is the swelling ratio of the chain (relative change of the linear dimensions), C_1 is the parameter related to the polymer structure and molecular weight of the solvent, Z

is the number of segments in the Gaussian chain, and χ is the Flory-Huggins parameter. The physical meaning of this equation is transparent: the left-hand side is related to the energy of elastic deformation (expansion and contraction, respectively), and the right-hand side represents the energy of polymer-solvent interaction. Therefore, it can be applied to more complex swelling systems, such as those considered in this work.

Table 1: Solvents discussed in the current work, following Ref. 6, which include not only battery electrolyte solvents, but other organic solvents of different quality with respect to PP. This set of solvents allows us to explore a broader space of the Flory-Huggins parameter values. Thickness d of the polypropylene films immersed in these solvents,[6] $\epsilon_{\perp} = d/d_0$, $d_0 = 24.23\,\mathrm{um}$, and Flory-Huggins parameters for PP-solvent pairs calculated using the UNIFAC-FV method at 25 °C.

Solvent	d, um	$\epsilon_{\perp}$	χ
Perfluorooctane (PFO)	23.89	0.986	3.800
Decane	24.67	1.018	0.130
n-Pentane	24.57	1.014	0.292
Hexane	24.37	1.006	0.242
n-Heptane	24.58	1.015	0.206
Octane	24.69	1.019	0.169
Cyclohexane	25.17	1.039	0.083
Cyclopentane	25.18	1.039	0.129
Diethyl Carbonate (DEC)	24.33	1.004	1.483
Toluene	24.82	1.025	0.374
Ethyl Acetate	24.41	1.008	1.202
Acetone	24.26	1.001	1.986
Dimethyl Carbonate (DMC)	24.12	0.996	1.924
Acetonitrile	24.24	1.001	3.066
Propylene Carbonate (PC)	23.91	0.987	3.700

While the Flory-Huggins theory[11,12] was initially derived for dilute polymer solutions, it can be applied to rubber-like polymers in solvents.[13–15] The separator films are strongly anisotropic; however, experiments report only swelling in one dimension (Fig. 1), the change of the separator thickness d, with respect to the thickness of the dry sample d_0.[5] Therefore, it is natural to relate the measured strain, normal to the separator plane $\epsilon_{\perp} = d/d_0$, to the swelling ratio α, and we will simply assume $\epsilon_{\perp} = \alpha$. Table 1 gives the values of measured thickness d of polymer films immersed in a range of solvents (data from Ref. 6), $\epsilon_{\perp}$ calculated

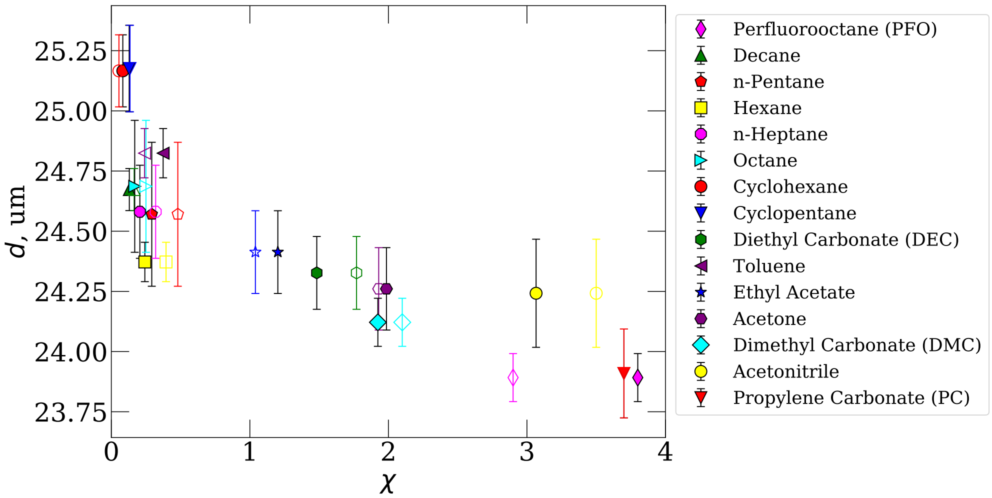

Figure 1: Experimental data for thickness is taken from Ref. 6. The two data sets are plotted for different χ values. The data set with solid markers show the experimental data measured at room temperature as a function of Flory-Huggins parameters calculated in this work using UNIFAC-FV. The data set with empty markers show the same experimental d as a function of Flory-Huggins parameters calculated in Ref. 6, which had an error in the calculation. The same marker shapes and colors correspond to the same solvents. The error bars represent the experimental uncertainties because of the thickness d of the PP separator in various solvents as a function of the Flory-Huggins parameter χ.

from these data, and the Flory-Huggins parameters calculated from the polymer activity coefficient a_1 using equation[10]

$$\ln\left(\frac{a_1}{\phi_1}\right) - \left(1 - \frac{1}{x}\right)\phi_2 = \chi\phi_2^2 \tag{2}$$

where ϕ_1 and ϕ_2 are the polymer and solvent mole fractions, and x is the degree of polymerization. The activity coefficient, a_1, in its turn, is found using the UNIFAC-FV model. UNIFAC (Universal Functional-Group Activity Coefficient) is a method to predict the activity of systems.[16] This method represents the activity coefficient a_1 of the solvent in a binary mixture by two parts, the combinatorial and the residual part. The combinatorial part considers the activity contribution due to differences in the size and shape of the molecules; the residual part considers the energy interactions, functional group sizes, and interaction surface areas. UNIFAC works well for most systems with small molecules. However, polymer molecules are large, and the free volume contribution to the overall activity is significant. Hence, a third term, representing the free volume, is introduced in the equation for the activity coefficient.[17]

$$\ln(a_1) = \ln\left(a_1^{\mathrm{C}}\right) + \ln\left(a_1^{\mathrm{R}}\right) + \ln\left(a_1^{\mathrm{FV}}\right) \tag{3}$$

For details of the calculations and the parameters used, see Supporting Information.

Eq. 1 has a trivial solution of $\alpha = 1$, i.e. no swelling at $\chi_{\mathrm{c}} = 1/2$, which is known as a theta point.[10,18] However, the data in Table 1 shows that the experimental $\alpha = 1$ corresponds to a different, noticeably higher value of the Flory-Huggins parameter. Since Eq. 1 captures the basic physics of polymer swelling, we assume that it is still applicable to the porous films considered here, but the value of the Flory-Huggins parameter is shifted by a constant $\Delta\chi$. We attribute this constant shift to the microstructure of the polymer film, such as porosity and semicrystallinity. We can rewrite Eq. 1 as

$$\alpha^5 - \alpha^3 = \tilde{v}\left(\tilde{\chi}_{\mathrm{c}} - \chi\right) \tag{4}$$

where

$$\tilde{v} \equiv 2C_1 Z^{1/2}. \tag{5}$$

and

$$\tilde{\chi}_{\mathrm{c}} = \frac{1}{2} + \Delta\chi \tag{6}$$

Our hypothesis suggests that for a given polymer and a range of solvents, the left-hand side of Eq. 4 should be a linear function of the Flory-Huggins parameter χ. If it is the case, the two parameters of Eq. 4, $\tilde{v}$ and $\tilde{\chi}_{\mathrm{c}}$, along with the Flory-Huggins parameters for the PP-solvent pairs, fully predict the polymer swelling.

Results

Figure 2 shows the left-hand side of Eq. 4, calculated based on the experimental data for the thickness d of the Celgard 3501 separator, assuming $\alpha = \epsilon_{\perp}$, as a function of the Flory-Huggins parameter. As expected, the $\alpha^5 - \alpha^3$ shows nearly a linear trend as a function of χ. The solid line represents the linear fit, which includes all the data points except for the two solvents: cyclohexane and cyclopentane. Immersion of polymer separators in all solvents, except these two, did not cause irreversible changes in polymer samples' elasticity. These two solvents, however, not only showed the maximum swelling but also partially dissolved the polymer so that after removing the solvent and drying, the initial Young's moduli of the films were not recovered.[6] Partial dissolution of the polymer in these two solvents make them qualitatively different, therefore we considered them outliers for the regression.

The linear fit shown in Figure 2 provides the two dimensionless parameters of Eq. 4: $\tilde{v} = 0.0162$ and $\tilde{\chi}_c = 2.245$. The latter gives the shift of the theta-point to the values of higher Flory-Huggins parameters. The theta-point, which corresponds to the solvent which does not cause any swelling, is shown by the vertical dashed line in Figure 2.

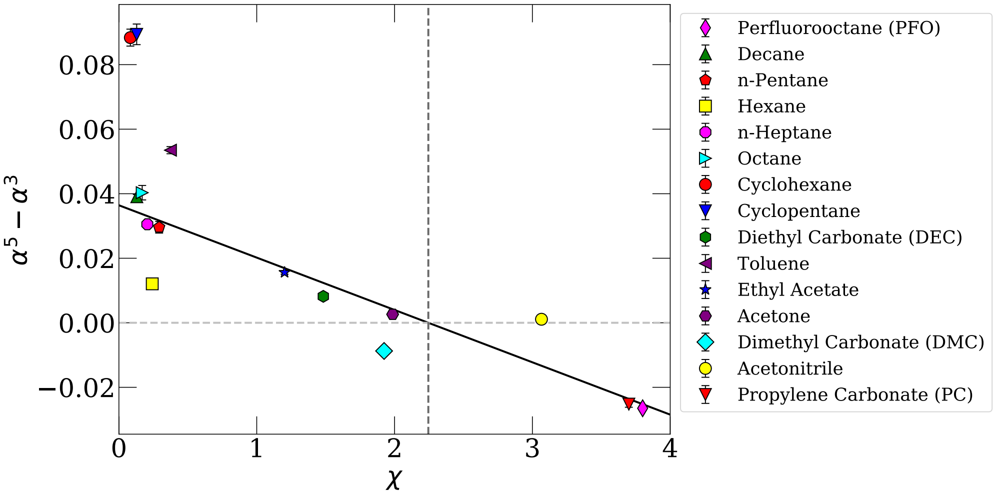

Figure 2: The dependence $\alpha^5 - \alpha^3$ calculated from the experimental swelling data[6] on the Flory-Huggins parameter χ for the PP-solvents. The solid line represents the linear fit (excluding cyclohexane and cyclopentane); the horizontal dashed line corresponds to $\alpha = 1$, i.e., the dry film; the vertical dashed line corresponds to $\tilde{\chi}_c = 2.245$.

This linear dependence suggests that one can predict swelling of the same separator type in a new solvent. In order to do that, one can simply calculate the χ parameter based on the UNIFAC-FV model, and using the parameters $\tilde{v}$ and $\tilde{\chi}_\mathrm{c}$ given above, calculate α from Eq. 4. Note that the script for the UNIFAC-FV model is provided in the Supporting Information.

The preceding experimental study[6] focused on pure solvents, so does this work. However, LIBs often utilize a mixture of different carbonates; in particular, ethylene carbonate (EC) is one of the widely used components.[19] Separator swelling experiments with pure EC at room temperature are not feasible since its melting point is 39 °C, however, our model can be used to estimate the χ parameter for EC and the hypothetical swelling. Using the liquid EC density at 39 °C, we got $\chi = 2.063$ at 25 °C, and $\chi = 1.992$ at 40 °C, suggesting that EC is close to the $\tilde{\chi}_\mathrm{c}$ and should not induce much separator swelling. EC is often used as a 1:1 mixture with DMC,[5] and since they have very close χ, the effect of EC-DEC mixture on the separator can be estimated based on the data for pure DEC (Table 1).

An alternative formulation for Eq. 1 can be written in terms of the temperature (referred to as Flory-Krigbaum theory[18]), and reads:[10]

$$\alpha^5 - \alpha^3 = C\psi\sqrt{Z}\left(1 - \frac{\theta}{T}\right), \tag{7}$$

Where ψ is the interaction entropy, and θ is the theta temperature. While Eq. 1 suggests that for a given polymer, at a given temperature, there could be different solvents: a good solvent causes polymer swelling ($\alpha > 1$), a poor solvent causes polymer contraction ($\alpha < 1$), and a theta-solvent corresponding to no volumetric change of a polymer ($\alpha = 1$). Alternatively (Eq. 7), for a given polymer and a given solvent, if a temperature is altered, the same polymer-solvent pair can show different behavior: the same solvent can be a good solvent or a poor solvent, depending on the temperature. The shift of the theta point introduced in our model (Eq. 6) can result in a different behavior with respect to temperature and is worth studying in more detail. However, it would require experimental data on the same polymers in solvents at various temperatures.

Discussion

Swelling of the separator due to interactions with the electrolyte solvent affects the battery performance in various ways. The first direct way is related to the effect of the separator strain on the ionic current through it. It is similar to the effect of external mechanical load on the separator, studied by Cannarella and Arnold,[20] both external load[20] and separator swelling, considered here, result in the pore shrinkage, and decrease of porosity as shown in Figure 3. Sufficient porosity of the separators is needed to absorb electrolytes, thereby reducing the ionic resistance and allowing Li ions to pass. However, separators cannot be overly porous as high porosity reduces mechanical properties leading to dendrite piercing.[1,21] For this reason, most commercial separators have a porosity of around 40 %, and small deviations in porosity have been shown to have significant effects on resistance.[1] Below we estimate the change in the resistance or the separator as a result of swelling.

The electrical resistance or the separator immersed in the electrolyte solution R, can be estimated based on the resistivity equation modified for porous media:[20]

$$R = \rho \frac{\tau d}{\phi A} \tag{8}$$

where ρ is the resistivity of the electrolyte, τ is the tortuosity of the separator material, A is the area of the separator, d and ϕ are the separator thickness and porosity, which were introduced above. When the separator swells in a constrained cell, the thickness d and the area A remain constant, but the porosity decreases due to the increase of the polymer volume V_{p}, as shown in Figure 3.

The initial porosity of the separator is defined as $\phi_0 = 1 - V_{\mathrm{p},0}/V_{\mathrm{t}}$, where $V_{\mathrm{p},0}$ is the volume of the dry (non-swollen) polymer, and V_{t} is the total volume occupied by the separator. Assuming that in the constrained cell, the V_{t} is constant, the porosity of the swollen separator

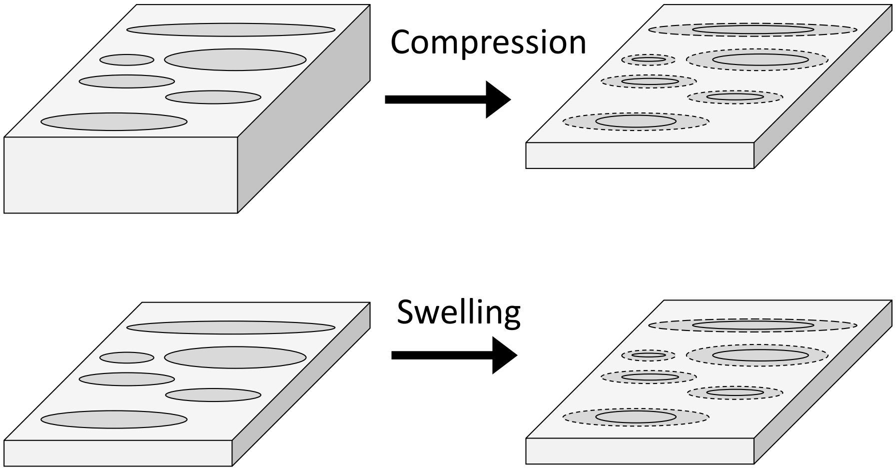

Figure 3: Schematic of separator in the absence of swelling, and swollen when constrained in a battery cell, which results in a decrease of porosity.

is $\phi = 1 - V_\mathrm{p}/V_\mathrm{t}$. The volume of the polymer in the swollen state V_p, assuming isotropic swelling, is related to the dry volume $V_{\mathrm{p},0}$ through the linear strain ϵ as $V_\mathrm{p} \simeq (1+3\epsilon)V_{\mathrm{p},0}$, therefore the porosity of the swollen separator is given as

$$\phi = 1 - (1+3\epsilon)(1-\phi_0). \tag{9}$$

Change in porosity affects the resistance given by Eq. 8 directly, as well as through the change of the tortuosity given by the Bruggeman relation[22,23]

$$\tau = \gamma\phi^{1-\alpha}. \tag{10}$$

Eq. 8 and Eq. 10 give the following resistance for the separator in the non-swollen state:

$$R_0 = \rho\frac{\gamma\phi_0^{1-\alpha}d}{\phi_0 A} = \rho\frac{d}{A}\gamma\phi_0^{-\alpha}. \tag{11}$$

An equation similar to Eq. 11 can be written for the resistance R of the separator in the swollen state (with the reduced porosity ϕ), therefore their ratio is

$$\frac{R}{R_0} = \left[\frac{\phi}{\phi_0}\right]^{-\alpha} = \left[\frac{1}{\phi_0} - (1+3\epsilon)\left(\frac{1}{\phi_0} - 1\right)\right]^{-\alpha} = \left[1 - 3\epsilon\left(\frac{1}{\phi_0} - 1\right)\right]^{-\alpha}, \tag{12}$$

where we utilized Eq. 9. At small deformations Eq. 12 can be also approximated as $R/R_0 \simeq 1+3\epsilon\alpha(1/\phi_0 - 1)$. Note that Eq. 12 agrees with the experimental data on change in resistance of a separator as a result of compressional stresses.[20] Using the values of porosity $\phi_0 = 0.515$ and the exponent $\alpha = 3.33$ from Ref. 20 in Eq. 12, we see that even $\epsilon \sim 1\%$ results in 10% increase of the resistance. This effect can be further amplified by the compressional stresses discussed in Ref. 20.

In addition to directly affecting the conductivity, swelling of the separator results in its plasticization – a reduction of its mechanical properties. Recent experiments showed that when separator materials are immersed in carbonate solvents used in LIBs, the solvents significantly reduce the mechanical properties of the polymers: tensile Young's modulus of the PP separator decreases by 50% upon immersion, so does the flow stress responsible for the failure of the materials.[5,24–27] These effects can have an even more substantial impact on the battery performance but are harder to quantify and require coupled electrochemical-mechanical models.[28]

We considered swelling of separator in various pure solvents, however, in a battery the separator is immersed in an electrolyte solution (lithium salt in one solvent, or in a mixture of solvents). To our knowledge the effects of salts on swelling have not been assessed, but the effects of salts on plasticization were tested in several papers.[5,24,29] Plasticization of separators in electrolyte solution (1M $LiPF_6$ in mixed carbonate solvents) was practically the same as in a pure solvent, in the absence of salt. The correlation between plasticization and swelling suggests that salts would not affect swelling either.[6] Therefore, experiments in Ref. 6 did not use salts when measuring plasticization and swelling of the separator, and we focused on the same systems here, developing a model for pure solvents. However, our model can be further extended to predict swelling in mixed solvents based on extensions of the Flory-Huggins theory for mixtures.[30–32]

The effects of solvent on swelling and plasticization of separator materials are not specific to the materials considered in Ref. 6 and here. Recent studies showed similar microstructure and mechanical properties for other brands of commercially available polyolefin separator materials,[33] so we expect our model to apply to those as well. However, the model will require reparameterization for separator materials different than the one considered in Ref. 6 and the current work. Experimental measurements of swelling in two different solvents will be necessary (and sufficient) to predict swelling in other solvents. To minimize the error in predictions, the two solvent-polymer pairs should have vastly different values of the Flory-Huggins parameter. This will likely be secured by choosing solvents with different chemical groups. Note that a recent experimental study[34] showed that the commercial cellulose-based separators show similar swelling and weakening behavior as polyolefins; we expect our model could also apply to those materials. Furthermore, much work in recent years has been focused on developing new battery separator materials,[35–37] while only a few of them[35] assess the new materials for swelling and softening in the presence of electrolyte solvents. Our model can help make such an assessment with minimal experimental effort.

Lastly, the separator is not the only polymer component of a typical lithium-ion cell. Several studies have shown that electrolyte solvents can affect the polymer binders used for electrodes.[38–40] This is another system where the proposed model can be useful. Overall, our model should help to include the effect of swelling of the soft components into multiphysics models for lithium-ion cells.[28,41]

Conclusion

We revisited the experimental data on polypropylene separator swelling in various solvents and came up with a model which relates the observed swelling to the Flory-Huggins parameter for the PP-solvent pairs. The model involves two parameters related to the polymer material's microstructure and cannot be obtained based on its molecular structure. In order to calculate these parameters, experimental measurements of swelling in two different solvents are necessary. Once these two points are available, the swelling can be predicted for any solvent based on the Flory-Huggins parameter. The Flory-Huggins parameters can be calculated using the UNIFAC-FV model; the Python implementation of this model is provided as Supporting Information with this article so that others can use it. Our model can be used for a quick assessment of various polymer-solvent pairs for application in lithium-ion batteries. However, a systematic study of various separators and a more advanced model are probably still needed.

Associated Content

The Supporting Information is available free of charge at `https://pubs.acs.org/`
The detailed description of the UNIFAC-FV method and its parameterization (PDF). The Python code UNIFAC-FV method (ZIP).

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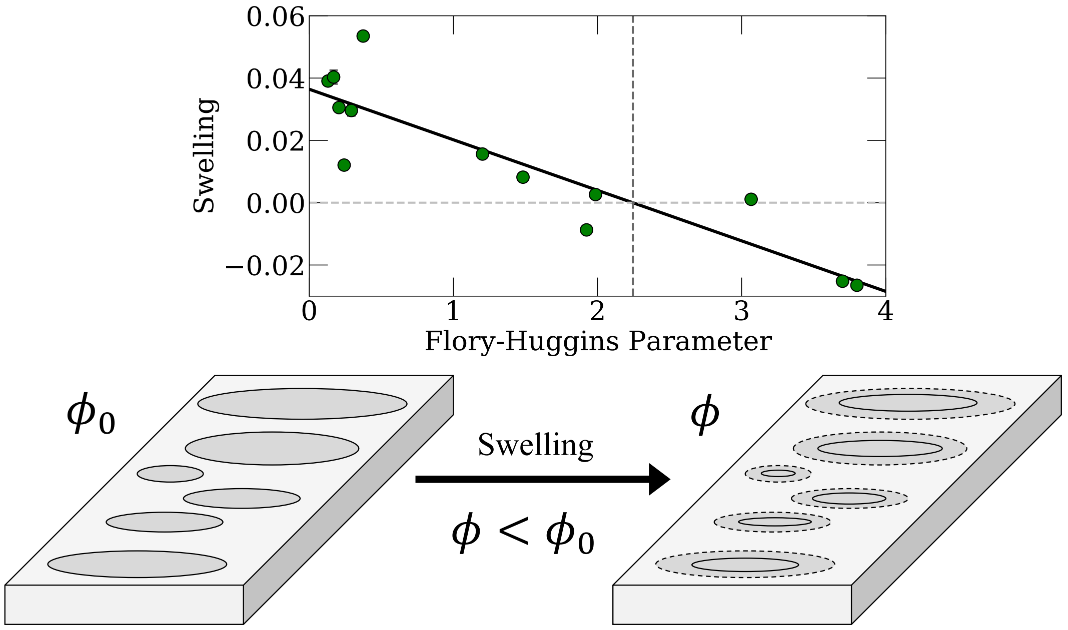

Figure 4: TOC Graphics