APPLICATION **NOTE**

Batteries – DSC / Kinetics Neo Software

Kinetic and Thermal Stability Analysis of an LiPF$_6$/EMC+DMC+EC Electrolyte for Lithium-Ion Battery Application

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Introduction

Lithium-ion batteries (LIBs) are the backbone of modern portable electronics, electric vehicles, and grid storage systems [1]. Among the essential components of LIBs, the electrolyte plays a critical role in determining performance, safety, and lifespan. One of the most widely used lithium salts in commercial electrolytes is lithium hexafluorophosphate (LiPF$_6$), primarily because of its good ionic conductivity and compatibility with graphite anodes. However, LiPF$_6$ is known to exhibit thermal and chemical instability, particularly under elevated temperatures.

The selection of solvents further complicates the stability profile of the electrolyte. Commonly used organic carbonate solvents ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) each contribute differently to the thermal behavior and decomposition pathways of the electrolyte system. Therefore, a detailed understanding of the kinetic and thermal stability of LiPF$_6$ in these solvent environments is crucial for improving battery safety.

This study aims to investigate the thermal stability and conduct a kinetic analysis of LiPF$_6$ in a single mixed carbonate solvent system (EMC+DMC+EC in a 1:1:1 ratio), using Differential Scanning Calorimetry (DSC) and the Kinetics Neo software, and to assess the thermal stability, determine kinetic parameters, and perform prediction through simulation under different conditions. Such investigations are essential for improving the safety of lithium-ion batteries.

Measurement Conditions

DSC measurements were performed using a NETZSCH DSC under the measurement conditions listed in table 1. The DSC curves obtained are the basis for kinetic evaluation.

Table 1

Instrument	NETZSCH DSC
Crucible	Closed gold-plated, high-pressure-stable stainless-steel container, volume 27 µl
Sample mass	11.3 - 11.9 mg
Temperature range	30 - 500°C
Atmosphere	N$_2$
Heating rates	1, 2 and 5 K/min

NGB · Application Note 391 · EN · 0825 · Technical specification are subject to change.

Measurement Results and Discussion

Figure 1 depicts the DSC curves of 1 M $LiPF_6$/EMC+DMC+EC in a 1:1:1 ratio electrolyte at different heating rates of 1, 2 and 5 K/min.

$LiPF_6$/EMC+DMC+EC electrolyte reveals multiple thermal events above 190°C. At a heating rate of 5 K/min:

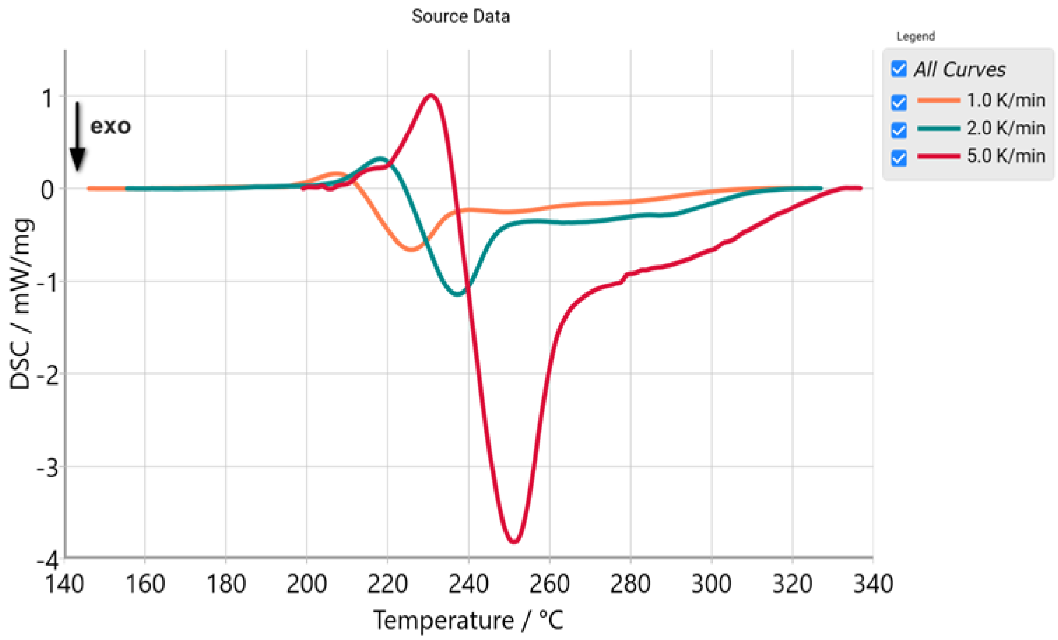
- an endothermal peak is observed at about 230°C,
- an exothermal peak appears at about 250°C,
- a broader, less intense exothermal peak emerges at about 290°C.

As the heating rate increases (1, 2, and 5 K/min), the DSC peaks shift to higher temperatures, accompanied by broader and less distinct peaks at higher heating rates (kinetic influence) [5].

Kinetic Analysis

Understanding the reaction kinetics of $LiPF_6$/EMC+DMC+EC electrolyte is essential for improving the safety of lithium-ion batteries. Thermal analysis reveals, at a heating rate of 5 K/min, an endothermal peak at about 230°C, attributed to the decomposition of $LiPF_6$ and solvent-specific interactions, particularly in the $LiPF_6$/DEC electrolyte system [2]. Following this, an exothermal peak appears at about 250°C, associated with the interaction between $LiPF_6$ and EC, where $LiPF_6$ may act as a Lewis acid by accepting electron pairs, promoting ring cleavage and forming decomposition products [2,3]. At higher temperatures, a broader and less intense exothermal peak is observed at about 290°C, which is possibly due to polymerization reactions that produce polyethylene oxide (PEO)-like polymers and release CO_2 [2,4].

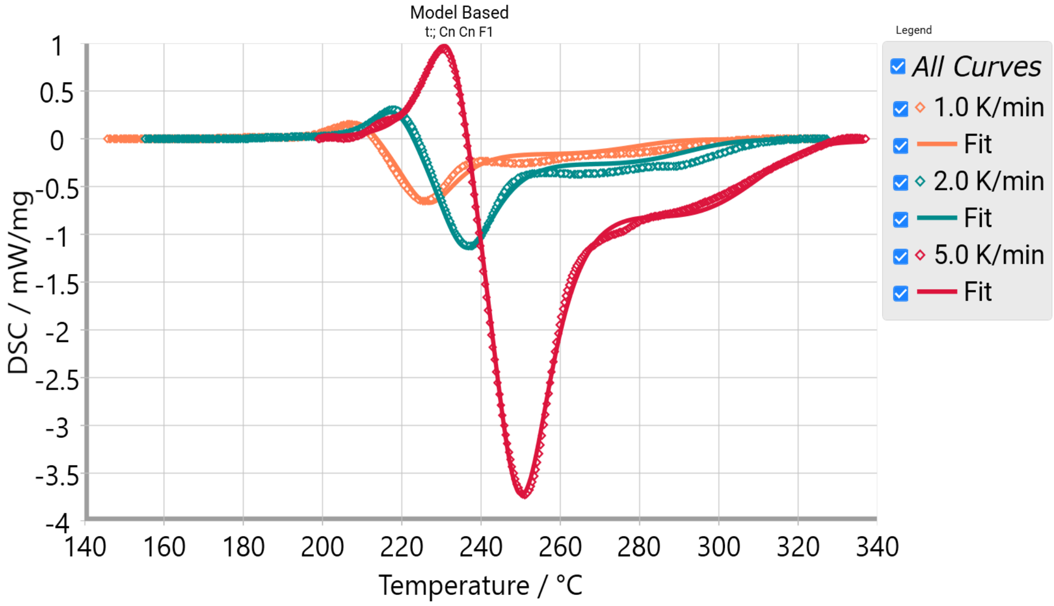
The dependence of endothermal and exothermal peaks on the heating rate allows for kinetic evaluation using the NETZSCH Kinetics Neo software.



1 DSC measurement on $LiPF_6$/EMC+DMC+EC electrolyte at different heating rates

Figure 2 shows the measurement of DSC curves as well as the curves calculated using the three-step kinetics model by using the NETZSCH Kinetics Neo software.

Table 2 summarizes the kinetic parameters. The results demonstrate strong agreement between the measured and calculated data with a coefficient of determination of 0.997.



2 Kinetic evaluation of DSC measurement on $LiPF_6$/EMC+DMC+EC electrolyte at different heating rates. Rhombus lines: measured curves; solid lines: calculated curves based on a three-step reaction.

Table 2 Kinetic parameters of $LiPF_6$/EMC+DMC+EC electrolyte DSC measurement

Reaction step	A→B	B→C	C→D
Reaction type	Cn	Cn	F1
Activation energy [kJ/mol]	146.3	137.2	118.6
Log (pre-exponential factor) [Log (1/s)]	12.3	10.9	8.6
Reaction order	0.89	1.94	1
Log (Autocat pre-exponential factor [Log(1/s)]	1.18	1.24	-
Contribution	-0.17	0.79	0.36
Coefficient of determination (R^2)		0.997	

Cn: Reaction of n^th^ order with autocatalysis
F1: Reaction of 1st order

The degree of conversion, α, is calculated by the Kinetics Neo software from the DSC measurement, where α ranges from 0 to 1 (see equation 1). In thermal analysis, the conversion is operationally defined as the thermoanalytical effect observed at temperature *T* (or at time *t* for isothermal measurements) divided by the total thermoanalytical effect. Specifically, for DSC, the observed thermoanalytical effect is heat consumption/evolution, so the definition of thermoanalytical conversion is as follows:

$$\alpha = \frac{\Delta H\ (T)}{\Delta H\ (total)} \quad (1)$$

where *ΔH (T)* is the partial area of the DSC peak up to temperature *T*, and *ΔH (total)* is the total area of the peak corresponding, to the complete enthalpy change of the reaction.

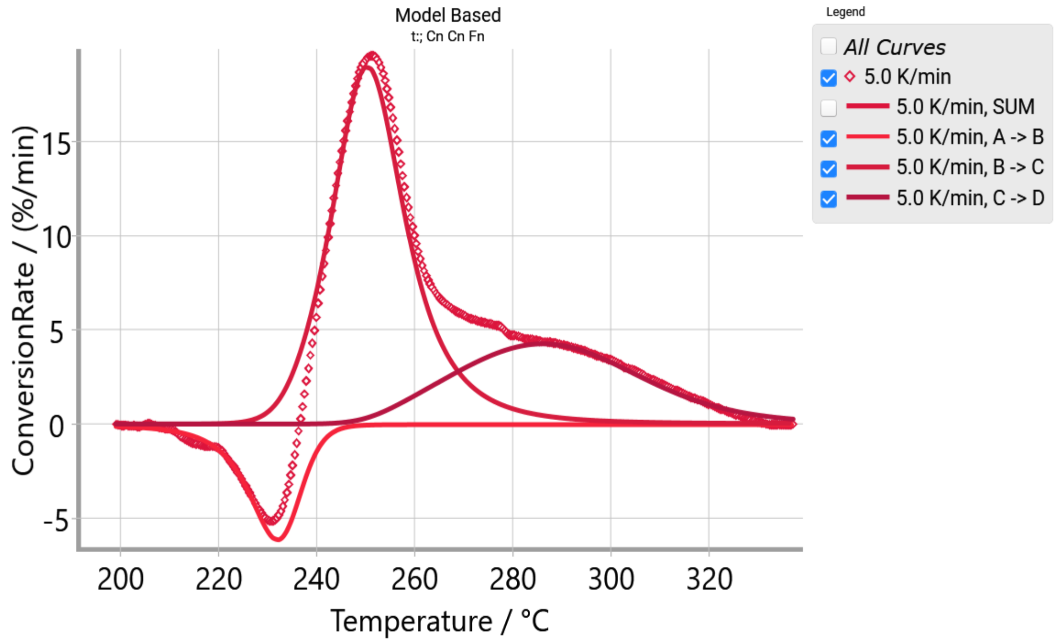
This suggests a multi-step reaction process, which can be modeled with a three-step kinetic model.

The reaction rate of each step j [5], is described by the function (eq. 2):

$$\text{Reaction Rate}_j = A_j . f(e_j, p_j) . e^{\left(-\frac{Ej}{RT}\right)} \quad (2)$$

A_j: pre-exponential factor
E_j: activation energy [J/mol]
T: temperature [K]
R: gas constant (8.314 J/K.mol)
$f(e_j, p_j)$: function dependent on the concentration of the initial reactant, e_j, and the concentration of product, p_j

For the DSC measurement on the $LiPF_6$/EMC+DMC+EC electrolyte, we observe three thermal events corresponding to the conversion rate peaks at about 230, 250 and 290°C as shown in figure 3, where the conversion rate (at 5 K/min) is defined as the first derivative of conversion with respect to time.

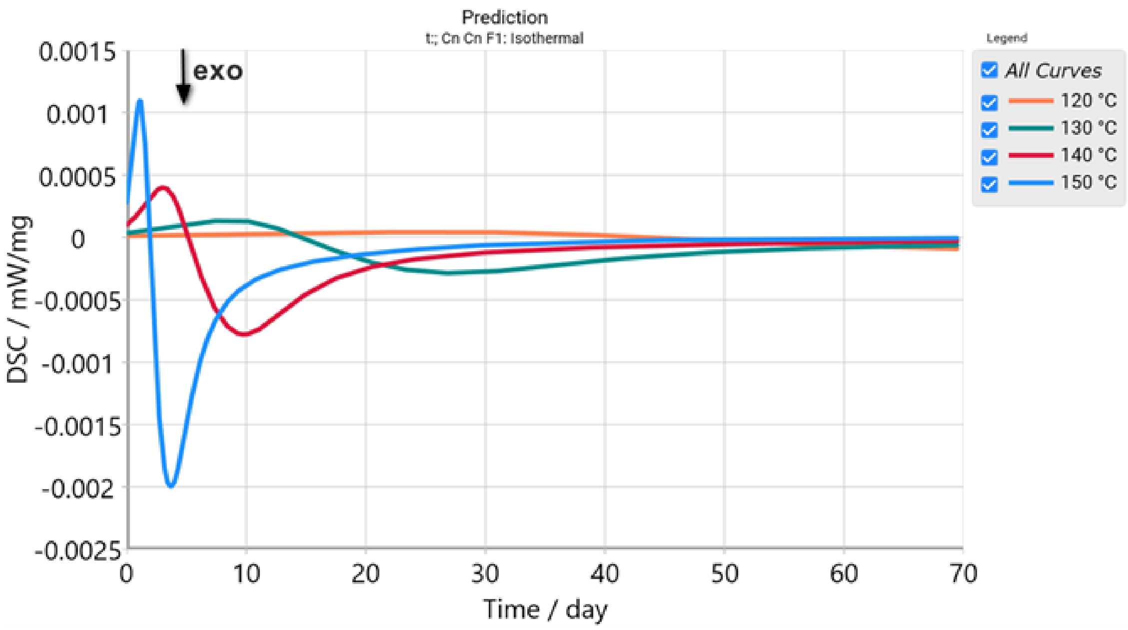


3 The conversion rate of the measurement at 5 K/min. Three peaks indicate three reaction steps. Rhombus lines: measured curves; solid lines:

Isothermal Prediciton Based on Non-Isothermal Kinetic Anallysis

Based on the determined kinetics model, the Kinetics Neo software calculates the behavior of the $LiPF_6$/EMC+DMC+EC electrolyte at any time/temperature.

Using the Kinetics Neo software, we can predict the reaction behavior of the $LiPF_6$/EMC+DMC+EC electrolyte at various temperatures. Figure 4 presents the $LiPF_6$/EMC+DMC+EC electrolyte's DSC signal under different isothermal conditions. At higher temperatures (150°C), sharp endothermal peaks appear rapidly (after around 1 day). As the temperature decreases to 140°C and 130°C, endothermal peaks appear at 3 days for 140°C and at 9 days for 130°C. At 120°C, a broader and less intense endothermal peak emerges after extended durations (~24 days). Figure 4 shows the prediction of the signal of the $LiPF_6$/EMC+DMC+EC electrolyte at 120°C, 130°C, 140°C and 150°C.



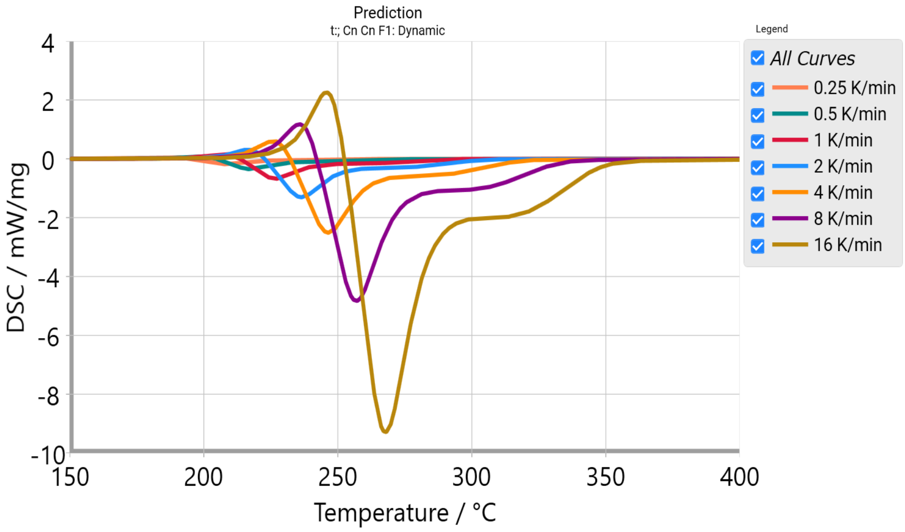
4 Prediction of the DSC signal of the $LiPF_6$/EMC+DMC+EC electrolyte at different isothermal conditions from 120°C to 150°C over 70 days.

Prediction at Different Heating Rates Using Non-Isothermal Kinecis Analysis

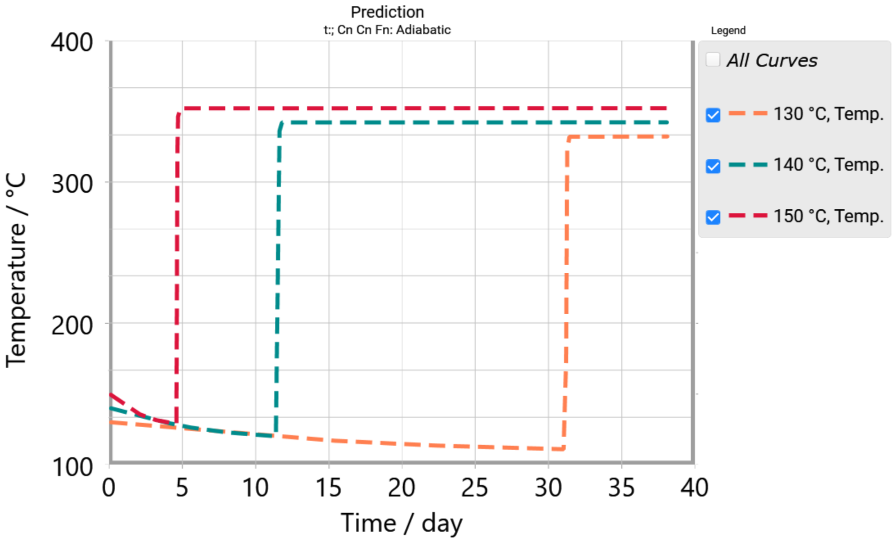
Figure 5 shows the prediction of DSC signals for $LiPF_6$ in an EC+DMC+EMC solvent at various heating rates as a function of temperature. This prediction clarifies the effect of the heating rate on electrolyte stability. Kinetics Neo software also enables predictions based on isothermal kinetic analysis.

Adiabatic Prediction Based on Non-Isothermal Kinetic Analysis

Figure 6 shows that the $LiPF_6$/EMC+DMC+EC electrolyte is predicted to undergo thermal runaway after approximately 4.5 days at 150°C, 11.5 days at 140°C, and 31.2 days at 130°C under adiabatic conditions. The initial decrease in the temperature curve is attributed to an endothermal reaction step. For the electrolyte, a median literature value of 1650 $J\,kg^{-1}\,K^{-1}$ was adopted for its specific heat capacity and the contribution of $LiPF_6$ was neglected, given its low mass fraction in the mixture [6]. The system was considered with an enthalpy of 333.65 $J\,g^{-1}$ and a temperature change (ΔT) of 202.2 K.



5 Prediction of the DSC signal of the $LiPF_6$/EMC+DMC+EC electrolyte as a function of temperature at different heating rates



6 Prediction of adiabatic temperature change of the $LiPF_6$/EMC+DMC+EC electrolyte under different adiabatic conditions with initial temperatures of 130, 140 and 150°C.

Conclusion

The combination of the NETZSCH DSC and the Kinetics Neo software has proven effective in determining the kinetic parameters of $LiPF_6$-based electrolytes and predicting thermal behavior through simulation at various temperatures, heating rates and adiabatic conditions. Such investigations are critical for ensuring the safety of lithium-ion batteries.

Literature

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