

# Toward Model Prediction for Combustion Properties of Lithium-Ion Battery Electrolyte Solvents

Keisuke Kanayama<sup>1,2</sup>, Hisashi Nakamura<sup>1</sup>, Takuya Tezuka<sup>1</sup>, Kaoru Maruta<sup>1</sup>

<sup>1</sup> Institute of Fluid Science, Tohoku University

Sendai, Miyagi, Japan

<sup>2</sup> Graduate School of Engineering, Tohoku University

Sendai, Miyagi, Japan

## 1 Introduction

Thanks to high energy density, carryable size and lack of memory effect, lithium-ion batteries (LIBs) are embedded in many products in our daily life, such as mobile phones and laptops. With the greater global interest in clean energy, the demand for larger-scale LIBs is growing in the energy storage systems and transportation industry [1]. A main concern of the use of LIB is, however, fire incidents. Since LIB is composed of flammable electrolyte solvents, thermal runaway triggered by mechanical, electrical and thermal abuses will lead to fire and, potentially, explosion under certain circumstances. During the thermal runaway event, electrolyte solvents are vaporized and ejected as gas or aerosol accompanying other partially reacted gas species [2]. For the electrolyte solvents, linear and cyclic carbonate esters, dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), ethylene carbonate (EC) and propylene carbonate (PC), are commonly used [1,3]. From an electrochemical aspect, EC is an essential component in LIBs to facilitate the dissociation of lithium salts owing to its large dielectric constant [1]. On the other hand, due to its high viscosity, EC, which is in solid phase at room temperature and ambient pressure, needs co-solvents that possess low viscosity such as the linear carbonate esters. There are a few studies on global combustion properties, i.e., ignition delay time and laminar flame speed, of DMC [4,5] and DEC [6,7] whereas data of EC or mixed solvents has not been reported to the best of the authors' knowledge. Our recent work on gas-phase EC/DMC pyrolysis using a micro flow reactor with a controlled temperature profile (MFR) [8] provided the first experimental data on speciation and chemical kinetic model that includes EC pyrolysis. As demonstrated by Harris et al. [2], simulating flame properties would be helpful to evaluate a relative suitability of the carbonate esters for the use of electrolyte solvents in LIB where flammability is in concern.

The aim of the present study is to demonstrate the gas-phase flammability of electrolyte solvents by simulating laminar flame speed as a representative global combustion property. First, updates in the chemical kinetic model for linear and cyclic carbonate esters are carried out to realize computations for EC oxidation and to improve model predictions. Then, laminar flame speeds of commonly used electrolyte solvents, EC/DMC, EC/EMC and EC/DEC, are simulated using the updated model in this study. Finally, flammability to be considered for the electrolyte solvents is discussed from the viewpoint of gas-phase combustion property.

## 2 Chemical Kinetic Model for Carbonate Esters: LIB Electrolyte Surrogate Model

To perform model predictions for combustion properties of the carbonate esters, previously constructed EC pyrolysis model [8], which includes pyrolysis and oxidation reactions of linear carbonate esters (DMC, EMC and DEC) [9], was updated. Firstly, according to a recent shock tube study on pyrolysis of DMC, EMC and DEC by Grégoire et al. [10], the base mechanism and some of the DMC-, EMC- and DEC-related reactions were updated. AramcoMech 1.3 was used as a base mechanism in the previous EC pyrolysis model while NUIGMech 1.1 [11] was adopted as a C<sub>0</sub>–C<sub>2</sub> base mechanism in the present study. This is because model predictions using NUIGMech 1.1 showed agreements fairly well with experimentally obtained combustion properties, e.g., ignition delay time and laminar flame speed, for H<sub>2</sub>/CO/CO<sub>2</sub>/C<sub>1</sub>–C<sub>3</sub> hydrocarbons mixed gas [10,12]. Reactions related to DMC, EMC, DEC and ethanol were also updated by Grégoire et al. [10] based on CO time-history profiles. Secondly, two initiation reactions of EC were added to the EC pyrolysis model to capable EC oxidation: EC = CY(CJOC\*OOC) + H (R1) and EC + O<sub>2</sub> = CY(CJC\*OOC) + HO<sub>2</sub> (R2). The reaction rate constants were analogically taken from 1,3-dioxolane [13], which is a five-member ring with two O-atom involved. Finally, several reactions mainly focusing on CO and CO<sub>2</sub> production were reviewed. Due to the chemical structure of carbonate esters, 1- or 2-step CO<sub>2</sub> production directly delivered from the parent molecule is a typical fuel consumption pathway. For instance, CO and CO<sub>2</sub> production pathways from EC pyrolysis are shown in Figure 1 (CY(COC\*OOC) denotes EC). The intermediates undergo CO, resulting in two different CO<sub>2</sub> pathways in the case of carbonate esters, fuel-to-CO<sub>2</sub> production and CO-to-CO<sub>2</sub> oxidation. Unimolecular decomposition reactions of carbonate esters are the key to CO and CO<sub>2</sub> prediction for the former, while the chemistry of the intermediates, especially oxygenates, would play an important role in the prediction for the latter. For DMC unimolecular decomposition reactions, as was suggested in a previous study [8], a theoretically obtained rate constant at 1atm by Zhang et al. [14] for DMC = CH<sub>3</sub>OCH<sub>3</sub> + CO<sub>2</sub> (R3) was used in the present study. In EMC and DEC pyrolysis, methanol and ethanol chemistry, respectively, were found to have a potential impact on time-dependent CO prediction [10]. Thus, acetaldehyde (CH<sub>3</sub>CHO) chemistry would be important for CO prediction in EC case. Figure 2 shows the rate constants and a branching ratio of unimolecular decomposition reactions of ethylene oxide (C<sub>2</sub>H<sub>4</sub>O1-2). Although there are seven decomposition pathways reported in the literature [15], two of them that are included in NUIGMech 1.1 are exhibited in Fig. 2. The rate constants of C<sub>2</sub>H<sub>4</sub>O1-2 = CH<sub>3</sub> + CO (R4) and C<sub>2</sub>H<sub>4</sub>O1-2 = CH<sub>3</sub>CHO (R5) are similar to each other in NUIGMech 1.1 whereas those theoretically obtained by Joshi et al. [15] indicate a difference of two orders of magnitude at 1200 K where R1 is dominant. The seven unimolecular decomposition reactions of C<sub>2</sub>H<sub>4</sub>O1-2 and their theoretical rate constants from the literature were applied to the present model. Modified reactions in this study are summarized in Table 1 and hereafter the updated model will be called as “LIB electrolyte surrogate model.” Figure 3 presents the comparison between predictions for EC pyrolysis products using the original EC pyrolysis model [8] and LIB electrolyte surrogate model updated in this study. Although there is no dramatic change in the predictions, the computational results using the present LIB electrolyte surrogate model show a slight improvement in most species at around 1100 K. For further validation and updates of the model, more pyrolysis and combustion experiments of EC need to be carried out.

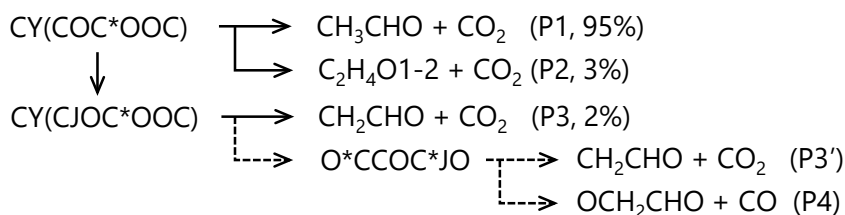


Figure 1: Possible CO and CO<sub>2</sub> production pathways from EC pyrolysis. Solid arrows (P1–3) depict major pathways appeared in EC/DMC pyrolysis at 1080 K where 30% of EC was consumed for the  $T_{w,\max} = 1200$  K case along with their contribution percentages in the parenthesis [8]. Broken arrows (P3' and P4) indicate other possible CO and CO<sub>2</sub> production pathways included in the EC pyrolysis model.

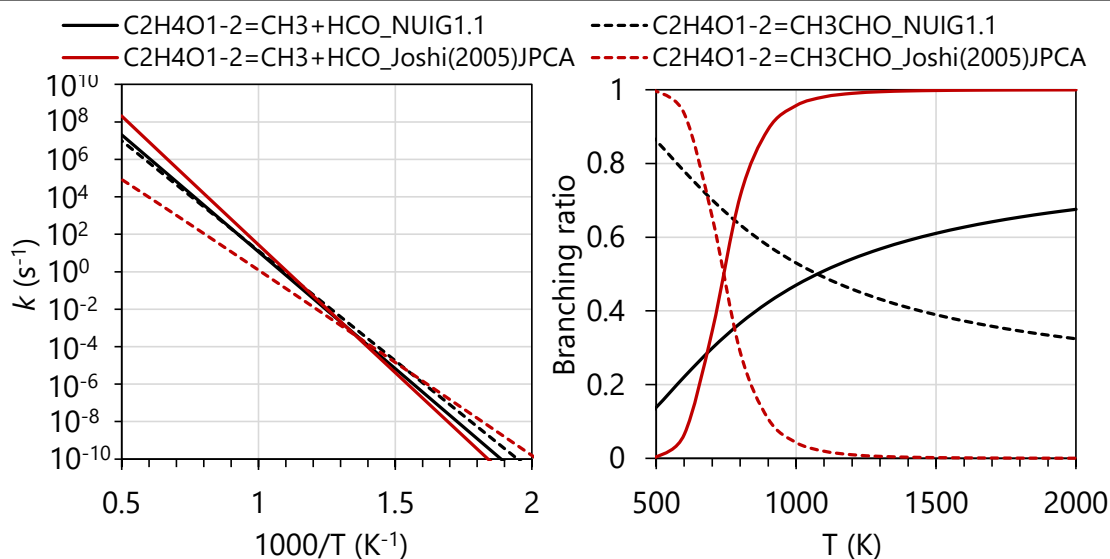


Figure 2: Rate constants of unimolecular decomposition reactions of ethylene oxide ( $C_2H_4O1-2$ ) adopted in NUIGMech 1.1 [11] (black) and theoretically calculated by Joshi et al. [15] (red). Five other reactions for the latter are not included in this figure, which account for up to 8% in total in the branching ratio at 2000 K.

Table 1: Modification in the LIB electrolyte surrogate model ( $k = AT^n \exp(-E_a/RT)$ , units in cal, mol and s).

No.	Reaction	A	n	$E_a$	Ref.
	Base mechanism: NUIGMech 1.1				[11]
	Ethanol, DMC, EMC and DEC reactions				[10]
R4	$C_2H_4O1-2 = CH_3 + HCO$	$5.57 \times 10^{13}$	0.400	61884	[15]
R5	$C_2H_4O1-2 = CH_3CHO$	$3.18 \times 10^{12}$	-0.760	46424	
	$C_2H_4O1-2 = CH_4 + CO$	$1.07 \times 10^{13}$	0.110	63783	
	$C_2H_4O1-2 = CH_3CO + H$	$2.43 \times 10^{13}$	0.250	65310	
	$C_2H_4O1-2 = CH_2CHO + H$	$1.84 \times 10^{13}$	0.200	71781	
	$C_2H_4O1-2 = CH_2CO + H_2$	$3.57 \times 10^{12}$	-0.200	63033	
	$C_2H_4O1-2 = C_2H_2 + H_2O$	$7.63 \times 10^{12}$	0.060	69531	
R3	$DMC = CH_3OCH_3 + CO_2$	$2.45 \times 10^{14}$	0.0	72694	[14] <sup>a</sup>
-R1	$CY(CJOC*OOC) + H = EC$	$1.00 \times 10^{14}$	0.0	0	[13] <sup>b</sup>
R2	$EC + O_2 = CY(CJOC*OOC) + HO_2$	$1.26 \times 10^7$	0.0	72694	[13] <sup>b</sup>

<sup>a</sup> Rate parameters were obtained by fitting the 2-parameter Arrhenius expression to calculated rate constants at 1 atm and 700–1400 K from the literature. <sup>b</sup> Analogy to 1,3-dioxolane.

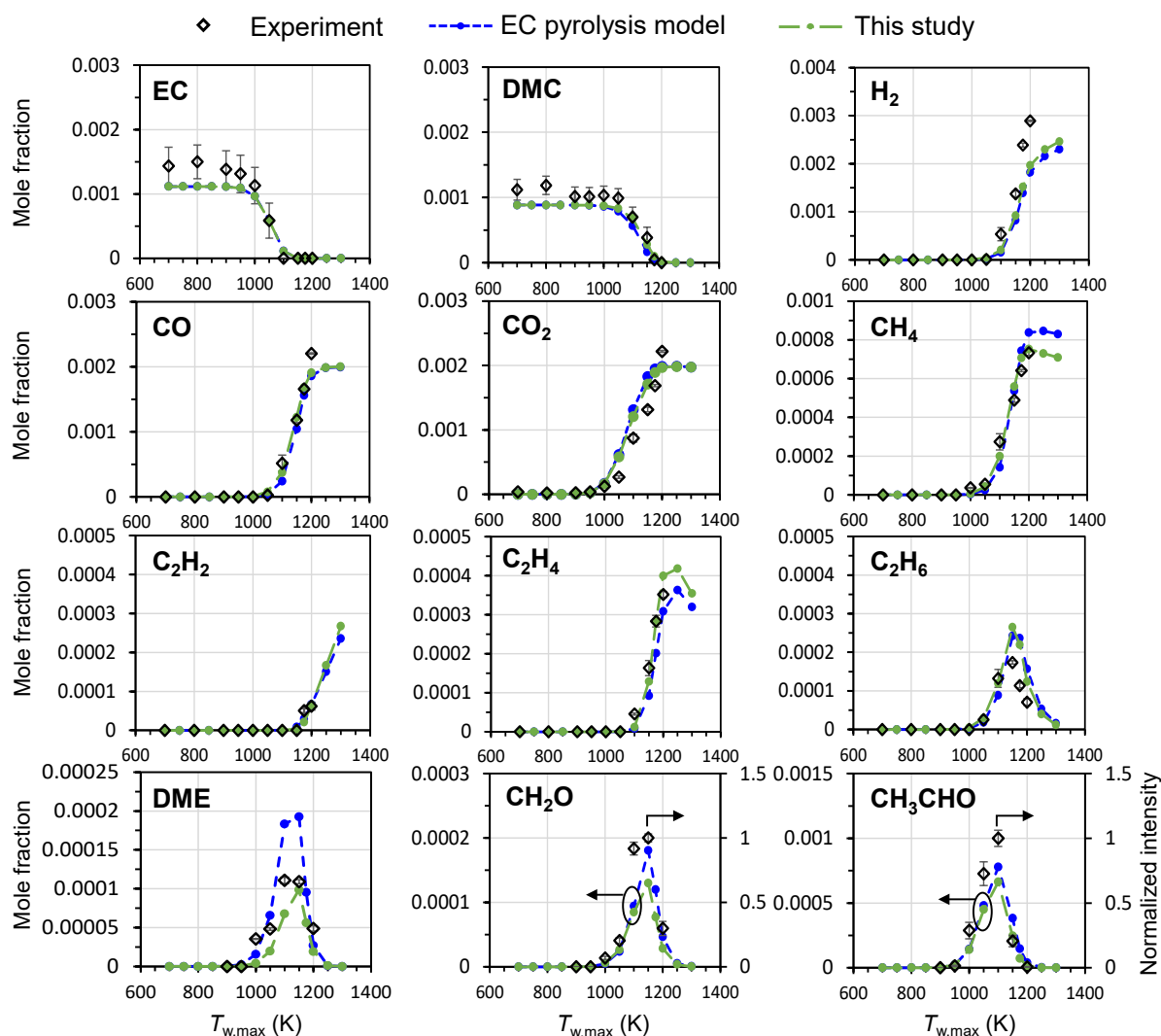


Figure 3: Model validation with speciation for EC/DMC pyrolysis in MFR. Experimental data and original model predictions (blue) from [8] and predictions using LIB electrolyte surrogate model (green).

### 3 Model Prediction for Global Combustion Parameters: Laminar Flame Speed

One of the most care-taking aspects of the LIB fire would be flame propagation after the thermal runaway event. Herein, laminar flame speed is simulated for commonly used electrolyte solvents, EC/DMC, EC/EMC and EC/DEC. 1-D adiabatic freely propagating flames were computed using PREMIX code in Chemkin-Pro. LIB electrolyte surrogate model was used as a chemical kinetic model. As representatives of the electrolyte solvents, EC/DMC/air, EC/EMC/air and EC/DEC/air mixtures were calculated. The compositions of the carbonate esters were all set as 1:1 in liquid weight ratio (Table 2). Inlet temperature and pressure were set to 500 K and 1 atm, respectively, by considering thermal runaway situations.

Figure 4 illustrates the computed laminar flame speeds of EC/DMC/air, EC/EMC/air and EC/DEC/air mixtures at equivalence ratio ( $\phi$ ) of 0.7–1.5. Interestingly, EC/EMC and EC/DEC show almost identical results, which are faster than EC/DMC by around 5 cm/s at  $\phi = 1.1$ . Computed adiabatic flame temperatures at  $\phi = 1.1$  were 2282, 2289 and 2299 K for EC/DMC, EC/EMC and EC/DEC, respectively. This implies that the fuel chemical structure would contribute to the flame speed through chemical

effects related to intermediate production, e.g.,  $C_2H_4$  from EMC and DEC. Although EC/DMC liquid is classified to be more “flammable” than EC/EMC and EC/DEC liquids based on flash point [3], the flame speed of a gas-phase EC/DMC mixture is slower than EC/EMC and EC/DEC mixtures. Thus, it is worth mentioning that the liquid flammability classification that largely relies on phase change may cause misleading in some cases. Along with the chemical kinetic modeling and simulations, experimental data on ignition and combustion properties of gas-phase electrolyte solvents is welcome to assess their fire hazard and to improve model capability.

Table 2: Composition of electrolyte solvents used in computations.

Solvent mixtures	Blending ratio (wt%)	Blending ratio (mol%)
EC/DMC	50/50	50/50
EC/EMC	50/50	54/46
EC/DEC	50/50	57/43

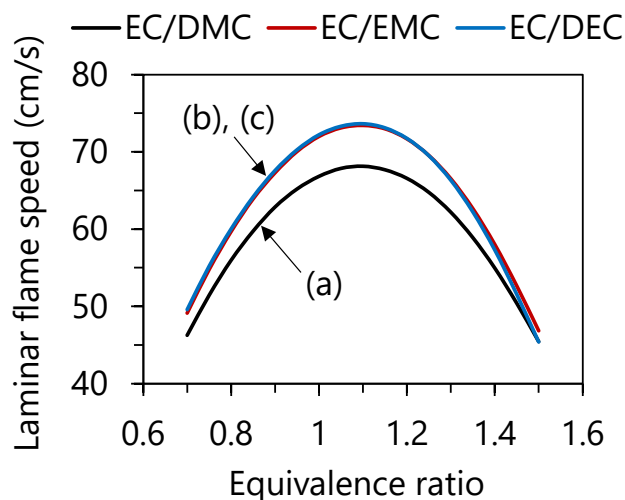


Figure 4: Computational laminar flame speeds of carbonate ester/air mixtures at 500 K and 1 atm as a function of equivalence ratio. Commonly used three different electrolyte solvents were subjected to simulate, (a) EC/DMC, (b) EC/EMC and (c) EC/DEC (50/50 wt% for all cases).

## 4 Conclusions

Chemical kinetic model for linear and cyclic carbonate esters (dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and ethylene carbonate (EC)) was updated based on literature aiming to be used for EC oxidation and to improve model predictions on combustion properties. To demonstrate the gas-phase flammability of lithium-ion battery (LIB) electrolyte solvents, laminar flame speeds of EC/DMC/air, EC/EMC/air and EC/DEC/air mixtures were simulated at 1 atm and 500 K using the updated model called as LIB electrolyte surrogate model. The computational flame speed of a EC/DMC/air mixture was found to be slower than those of EC/EMC/air and EC/DEC/air mixtures that showed almost consistent results to each other over the equivalence ratio of 0.7–1.5. This gas-phase flammability trend is the opposite of a liquid-base flammability classification that indicates EC/DMC liquid is more flammable than EC/EMC and EC/DEC liquids. By demonstrating the flame speed simulations for commonly used electrolyte solvents, the importance of investigating their ignition and combustion properties was argued.

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