

The Effect of Electron Beam Dosage in the Decomposition Behavior of Electrolytes Encapsulated Inside the Graphene Sheets Based on *In Situ* TEM Observation

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Real-time observation on the dynamics inside the battery can be an ideal way to obtain fundamental understanding about electrochemical reactions that can lead to rational design of electrode materials for the rechargeable batteries. In particular, *in situ* transmission electron microscopy (TEM) is the most suitable platform observing such dynamics as it can analyse the morphological, phase, electronic, and even chemical structure of respective elements [1].

To overcome the conventional *in situ* TEM set-up which had a significant limitation in either (1) using the solid electrolyte or ionic liquid electrolyte, which is distant from the cell condition (which uses organic electrolyte) or (2) limited high resolution imaging due to the considerable thickness of SiN_x window, graphene liquid cell GLC has been proposed as the alternative *in situ* TEM platform that can observe the dynamics in liquid with high resolution imaging [2]. GLC has also recently been used as the *in situ* TEM platform to observe various dynamics of electrode materials upon lithiation, such as the volume expansion of Si and growth dynamics of SEI layer [3,4]. Nevertheless, fundamental understanding about the effect that electron beam dosage has remains unclear. Since GLC uses electron beam (e-beam) irradiation to trigger lithiation [3,4], it is important to understand how the electron beam dosage actually affects the overall lithiation behaviour. In particular, understanding how the e-beam dosage critically affects the decomposition behaviour of organic electrolytes inside the graphene sheets is worth of research, as it can provide new insights for the further optimization in the *in situ* TEM observation using GLC.

To initiate our studies, we have categorized the different degree of e-beam dosage in a quantitative scale. For the electrolytes, a solvent mixture of 1.3 M of lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC):diethylene carbonate (DEC) (v/v = 3:7) with 10 wt% of fluoroethylene carbonate (FEC) was used. Table 1 exhibits the low, medium, and high electron beam intensity, expressed in e⁻ A⁻²s⁻¹. The maximum intensity was estimated to be about 5500 e⁻ A⁻²s⁻¹ as the *in situ* TEM observation was not viable at the intensity higher than 5500. Then the *in situ* TEM observation was conducted to understand how the electrolytes are decomposed at three different e-beam dosage states, as shown in Figure 1. In the low e-beam dosage, decomposition behavior of electrolytes is minimized. Although some electrolytes are decomposed at 725 and 832 s, no decomposition behavior was observed at 1150 s. In contrast, medium and high e-beam dosage allows more facile decomposition of electrolytes, where a number of decomposed electrolytes are clearly seen at different time scale. At high e-beam dosage, decomposition behavior of electrolytes was further activated, showing the presence of many decomposed electrolytes, with various sizes and shapes.

In summary, we have investigated the effect of e-beam dosage on the decomposition behaviour of organic electrolytes inside the GLC using by *in situ* TEM observation. It has been revealed through this study that e-beam dosage critically affects the overall decomposition behaviour of electrolytes, which needs to be taken into consideration when the future studies are conducted using GLC [5].

References:

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Relative Magnitude	Dosage Range ($e^- A^{-2}s^{-1}$)
Low beam intensity	1500-2000
Medium beam intensity	2500-3500
High beam intensity	4500-5500

Table 1. Categorization of electron beam dosage (low, medium, and high beam intensity).

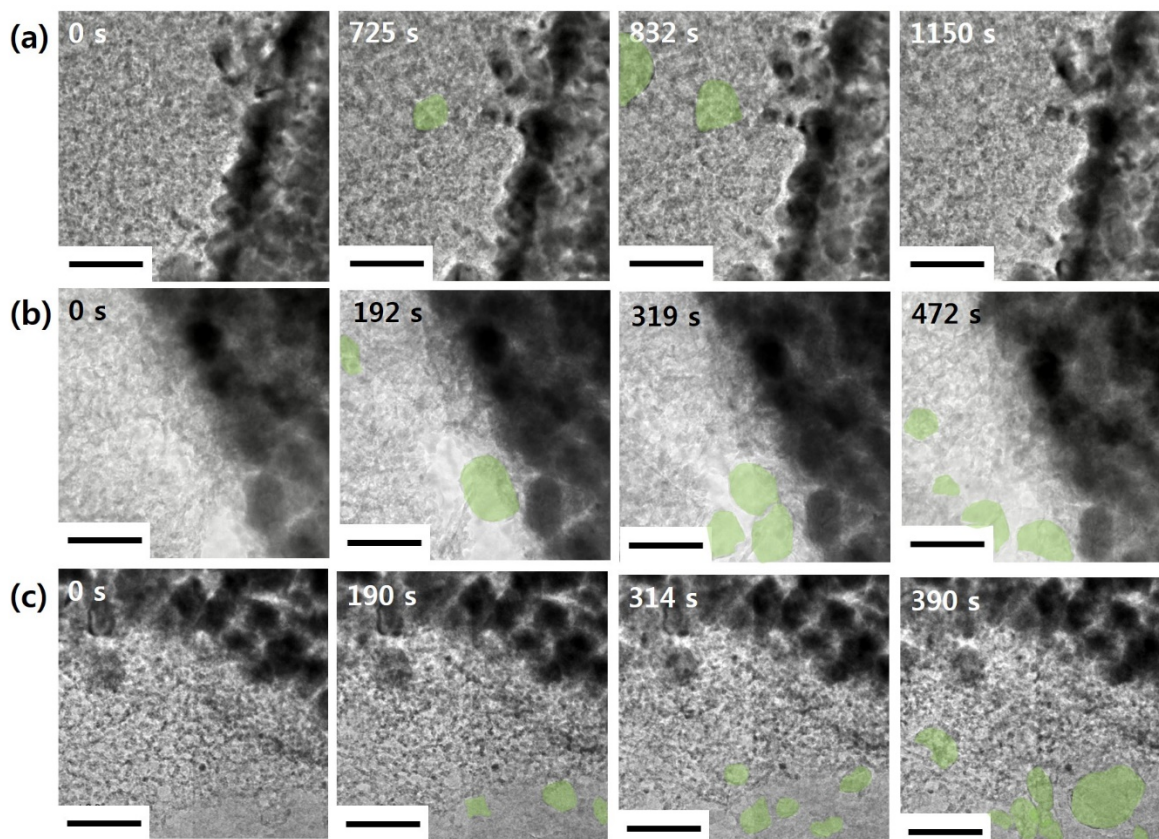


Figure 1. Time-series TEM images of decomposed electrolytes inside the graphene sheets in different electron beam dosage: (a) low electron beam dosage, (b) medium electron beam dosage, and (c) high electron beam dosage. (Scale bar = 100 nm)