

Deciphering the Chemical and Electrochemical Reactions of Li_2CO_3 in Li-ion Batteries using Online Electrochemical Mass Spectrometry

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Surface and interfacial decomposition reactions at the electrode/electrolyte interfaces are known to be key contributors which affect the cycling stability and capacity retention of Li-ion batteries. The build-up of surface impurities on the pristine electrodes and the formation of solid electrolyte interphase (SEI) on the anode and solid permeable interphase (SPI) on the cathode have been found critically altering the interphase morphology and stability [1]. Regardless the various experimental techniques which were developed and applied ex-situ to trace the changes in the interphase layers, it has not been fully understood how the surface species evolve chemically and/or electrochemically when interfacing the electrolyte. In this context, *operando* techniques which can monitor these reactions and their products, such as evolving gases, during operation of the cell would support the fundamental understanding of the stability of these surface species.

Here, we specifically explore the chemical and electrochemical decomposition reactions of Li_2CO_3 in alkyl carbonate electrolytes using ^{13}C -labeled Li_2CO_3 . Li_2CO_3 is a typical surface impurity on electrode surfaces post storage in air [2] and commonly found in the interphase layers during cycling [3]. In-depth investigations of the stability of ^{13}C -labeled Li_2CO_3 in contact with the Li salts, the electrolytes and during the electrochemical analysis were carried out, respectively. Using online electrochemical mass spectrometry (OEMS) to monitor the evolved gases, we are able to correlate the real-time reactions of Li_2CO_3 and LiPF_6 salt to produce CO_2 and POF_3 , also the voltage-dependent electrochemical decomposition of Li_2CO_3 in alkyl carbonate electrolytes (as shown in Figure 1).

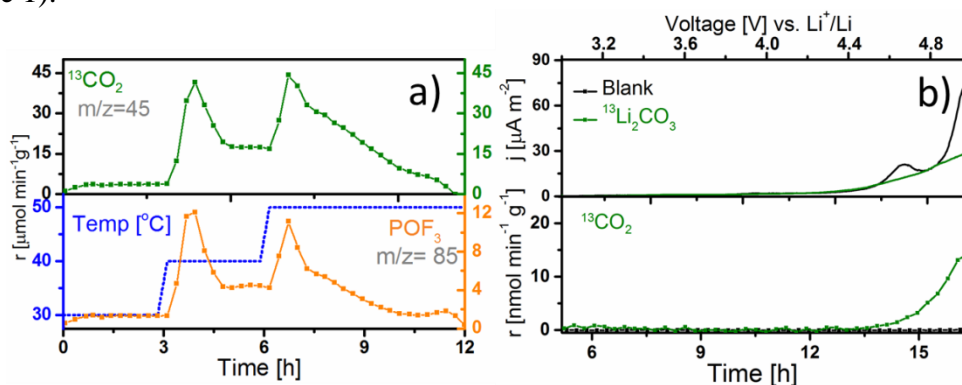


Figure 1. Gas evolution rate profiles of (a) $^{13}\text{CO}_2$ ($m/z = 45$) and POF_3 ($m/z = 85$) from ^{13}C -labeled Li_2CO_3 in contact with LiPF_6 salt between 30 and 50 °C; (b) $^{13}\text{CO}_2$ ($m/z = 45$) during the electrochemical analysis of ^{13}C -labeled Li_2CO_3 loaded glass carbon-based electrodes in LP47 electrolyte within 3.0–5.0 V vs. Li^+/Li at 30 °C.

References:

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