

Lithium alkyl carbonates: Preparation and investigation of stability

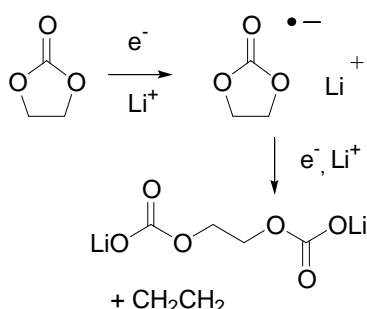
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The stability and reversibility of the lithium-ion batteries is dependent upon the electrolyte.¹ Organic Carbonates are the primary solvents used in lithium-ion batteries. However, organic carbonates are inherently unstable to the reduction potentials of the lithiated graphite anodes in lithium ion batteries. During the initial charging cycles, a solid electrolyte interface (SEI) is formed by reduction of organic carbonates on the surface of the anode in lithium-ion batteries. The SEI permits Li^+ migration into and out of the electrodes but prevents electron conduction.² Understanding the reactions that transform the organic carbonates into the SEI is essential for the development of better lithium-ion batteries. The generally held mechanism for reduction of carbonate solvents is a two step radical process which generates lithium alkyl carbonates and lithium dialkyl carbonates (Scheme 1).³ However, the anode SEI has poor stability at moderately elevated temperature ($> 50\text{ }^\circ\text{C}$) which leads to capacity fade in lithium-ion batteries. Developing a better understanding of the thermal and electrochemical decomposition reactions of the SEI components (lithium alkyl carbonates) will assist in the development of lithium ion batteries with improved calendar life.

In order to understand the structure of the components in the SEI, Lithium naphthalenide, a well known one electron transfer agent, was used as a model reducing agent for the lithiated graphite surface. Lithium naphthalenide is reacted with various carbonate solvents including ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) to generate the corresponding lithium alkyl carbonates in high yield.⁴ The products are analyzed by Nuclear magnetic resonance spectroscopy (NMR), Fourier transform Infrared spectroscopy (FTIR), and gas chromatography with mass selective detection (GC-MS). After characterization, the thermal stability of the lithium alkyl carbonates was investigated in the presence of carbonate solvents with and without added LiPF_6 . In addition, the stability of the lithium alkyl carbonates was investigated in the solid state by TGA and XPS. The synthesis, purification, and stability of lithium alkyl carbonates will be discussed.

Scheme 1

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