



# The Effect of Carbon Dioxide on the Cycle Life and Electrolyte Stability of Li-Ion Full Cells Containing Silicon Alloy

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Carbon dioxide is shown to be an effective additive to standard Li-ion electrolyte for extending the cycle life of full pouch cells containing an engineered silicon alloy. CO<sub>2</sub> was introduced to pouch cells by adding a few milligrams of dry ice to cells before sealing. The cells contained composite negative electrodes formulated with 15 to 17 wt% of an engineered silicon alloy and a LiCoO<sub>2</sub> positive electrode. Parasitic electrolyte reactions were measured in-situ by isothermal micro-calorimetry and high precision coulometry and compared to cells containing 1-fluoro ethylene carbonate (FEC). Extended cycling of cells containing CO<sub>2</sub> were compared to cells containing FEC. Cell gas generation and gas consumption were measured by applying the Archimedes principle. A new approach using small tubes in pouch cells to differentiate volume changes from gassing and solid expansion is introduced. Cells with CO<sub>2</sub> showed significantly lower parasitic thermal power, improved coulombic efficiency and better capacity retention compared to cells containing electrolytes with FEC. The gas generation/consumption experiments showed that Si alloy reacts with CO<sub>2</sub> during cycling until it is fully consumed. Combining FEC and CO<sub>2</sub> reduces the consumption rate of CO<sub>2</sub>. Microscopy of cross-sectioned cycled electrodes showed a thin SEI layer and minimal silicon alloy erosion. The combined work establishes CO<sub>2</sub> as a powerful precursor to an effective SEI layer on silicon alloys. Finally, CO<sub>2</sub> is shown to be an effective SEI former for graphite in EC-free electrolytes.

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The desire to increase energy density in Li-ion cells has fueled the research and development of silicon and silicon-based materials as a component of Li-ion negative electrodes. In most cases, however, only small amounts of silicon or silicon alloy are used largely because of the generally inferior cycle life of silicon compared to graphite. While there can be several reasons for the inferior cycle life of silicon and silicon alloys one important contributor to poor cycle life is the erosion of the silicon particle by parasitic electrolyte reactions.<sup>1-3</sup> Because of the volume changes Si experiences during cycling, continuous passivation is required at the surface and the demands on the electrolyte system are greater than for graphite.

Carbon dioxide (CO<sub>2</sub>) has been described as an effective electrolyte additive in metallic Li cells many years ago.<sup>4</sup> In that work it was shown that cycling efficiencies of the Li electrode were greatly increased in the presence of CO<sub>2</sub>. With the development of Li-ion cell chemistry the use of CO<sub>2</sub> was also explored early on.<sup>5-7</sup> In a few papers on the subject it was shown that the CO<sub>2</sub> generators, known as pyrocarbonates, were effective in forming SEI layers on graphite.<sup>8,9</sup> More recently a patent by workers at Sanyo has described the effect of electrolytes containing CO<sub>2</sub> on the cycle life of sintered negative electrodes containing silicon.<sup>10</sup>

In the course of our work on the erosion of silicon alloys our interest was drawn to the role of gas generation in cells of this type. It became apparent that CO<sub>2</sub> was remarkably effective as a precursor to an especially effective SEI layer on silicon alloys, significantly extending the cycle life. The effectiveness of CO<sub>2</sub> was also found to occur on graphite also but the effect is far less dramatic.

## Experimental

**Electrochemical cell construction.**—Machine wound pouch cells were used in this work. They were obtained from LiFUN Technology (Xinma Industry Zone, Hunan Province, China) as sealed dry cells. Two families of cells were tested in the context of this paper. Table I lists the attributes and formulations of the electrodes and cells. The cells that contain silicon alloy, LF129 and LF794, differ in the type of graphite used in the composite negative electrode and the composition and material mix of the conductive diluent. These differences may affect the mechanical failure mechanism from large volume changes of the Si alloy particles though the more significant difference is the

higher areal reversible capacity of LF794 at 3.3 mAh/cm<sup>2</sup> versus 2.6 mAh/cm<sup>2</sup> for LF129 cycled from 3.0 V to 4.25 V. The Si alloy used has a reversible capacity of 1180 mAh/g, a density of 3.5 g/cm<sup>3</sup>, a surface area of 6.9 m<sup>2</sup>/g and a median particle size of 5.2 μm. In cells not using CO<sub>2</sub> the cells were first opened in a dry room and dried at 70°C under vacuum overnight. The cells were then filled with 0.9 g of electrolyte in a dry room with an operating dew point of -50°C. The cell filling procedure employed brief, periodic vacuum degassing in order to allow the electrolyte to access all void volume within the cell's electrodes. The weight before and after the electrolyte filling procedure was recorded in order to ensure the weight of electrolyte added to each cell was consistent. The pouch cells were then sealed under vacuum in a MSK-115A vacuum sealing machine (MTI Corp.) The cells were allowed to stand for 24 hours prior to cycling to ensure complete wetting. In general no charge was applied during standing, in some cases, as noted, a 2 V hold was applied.

**Electrolyte preparation.**—The base electrolyte used in this work was 1 M LiPF<sub>6</sub> in a 3/7 (w/w) blend of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) obtained from BASF and used as received. Vinylene carbonate (VC) was obtained from Novolyte and 1-fluoro ethylene carbonate (FEC) was obtained from BASF and used as received. All solvents, salts and blends were stored in a dry box located within a dry room.

The introduction of CO

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**Table I. Specifications the of Li-ion pouch cells used in this study.**

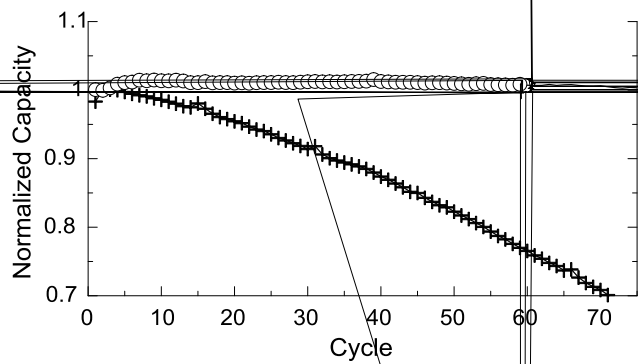
	LF129		LF794		LF44		LF45	
	Negative	Positive	Negative	Positive	Negative	Positive	Negative	Positive
Formulation (w/w)	BTR918/SiAlloy/ KS6/SP/LiPAA*	LiCoO <sub>2</sub>	MAGE/SiAlloy/ KS6/LiPAA	LiCoO <sub>2</sub>	Artificial graphite	LiCoO <sub>2</sub>	Artificial graphite	LiCoO <sub>2</sub>
	70.7/15/4/0.3/10	97	63/17/10/10	97	96	97	96	97
Coating weight (mg/cm <sup>2</sup> )	8.5	20.8	9.2	23.5	9.8	17.7	10	14.1
Nominal Porosity (%)	30	20	30	20	30	20	30	20
Current collector	15 um Cu	20 um Al	15 um Cu	20 um Al	10 um Cu	12 um Al	10 um Cu	12 um Al
Reversible capacity	2.6 mAh/cm <sup>2</sup> (3.0 V–4.25 V)		3.3 mAh/cm <sup>2</sup> (3.0 V – 4.25 V)		2.6 mAh/cm <sup>2</sup> (3.0 V - 4.3 V)		2.8 mAh/cm <sup>2</sup> (3.0 V–4.4 V)	
Balance cutoff voltage	4.35 V		4.35 V		4.4 V		4.5V	
Nominal capacity	220 mAh		290 mAh		250 mAh		240 mAh	

\*LiPAA-based binder.

are convenient for containing the CO<sub>2</sub> and the volume changes allow for straightforward characterization of consumption through volume changes.

**Archimedes measurements of pouch cell volume.**—Pouch cell volumes were measured using the Archimedes method.<sup>11</sup> Pouch cells were suspended from Mettler Toledo balances into beakers of pump oil. Weight measurements were logged using custom software from the balances and volumes calculated using the oil density. Pouch cells were wired using fine magnet wire to minimize the effect of the wires on the weight measurement. Balances and beakers were in a temperature controlled room held at 22°C and protected by a shroud to minimize the impact of air currents.

Volume measurements were also performed with pouch cells containing small open-ended polypropylene tub5.12(nd)-rom





Coulombic Efficiency  
Volume (ml)

1.0  
0.9  
0.9  
0.9  
0.9

2



graphite intercalation near the theoretical limit while under argon virtually no reversible capacity was found.<sup>6</sup> The surface chemistry