

## Study of Gas Evolution Reactions in Lithium-Ion Cells

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Generation of gaseous products during the formation, operation and storage of secondary lithium-ion cells poses a formidable technological challenge. Gasses released during the formation require an extra degassing process, thus increasing the production costs. Gas evolution during cycling of the formed cells, especially under overcharge conditions, leads to internal pressure build-up, performance degradation and potential safety failures. Gas generation during storage results in diminished shelf life of the product, particularly at elevated temperatures. The predicament is most challenging for cells packaged in soft foil laminate plastics due to the potentially unacceptable dimensional changes and package breach.

Despite the considerable attention, the mechanism of gas evolution is still very controversial. Extensive study of the anode surface chemistry and electrochemistry by D. Aurbach group [1,2] has established the major reaction paths of forming hydrogen, carbon monoxide, carbon dioxide and hydrocarbons, such as methane, ethylene and propylene. J. Kerr has proposed a mechanism explaining the carbon dioxide formation during storage at elevated temperatures, involving thermal decomposition of  $\text{LiPF}_6$  salt above 70 °C [3]. However, this mechanism does not explain gassing at lower storage temperatures or with electrolytes containing more stable anions, noted by H. Christoper and co-workers [4]. Taking into consideration the utmost importance of the problem, the significance and necessity of the study addressing the gassing mechanism is obvious.

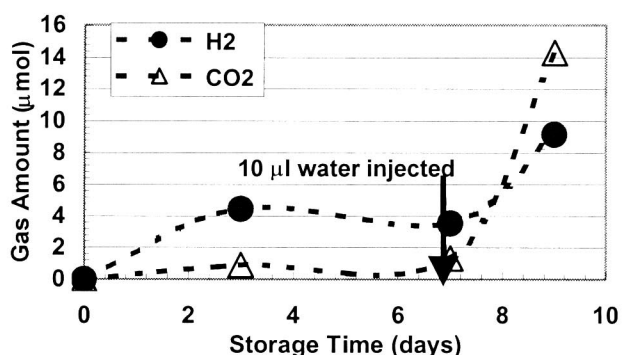
Our research of gas evolution reactions was performed in specially designed flooded electrochemical cells, containing a piece of MCMB-anode, a piece of  $\text{Li}_x\text{CoO}_2$ -cathode and an electrolyte of choice. Hydrogen, carbon monoxide and carbon dioxide were determined to be the major gaseous products, produced during storage of the cells. The amount of generated gas was proportional to the amount of water injected into the cell. Interestingly, the water addition resulted in simultaneous sharp increases in carbon dioxide and hydrogen formation (Fig. 1), with the carbon monoxide amount being virtually unaffected. Gas composition was found to depend on the cell OCV, carbon dioxide formation increasing relatively to hydrogen at lower voltage (Fig. 2.).

In an attempt to correlate the formation of each gas with reactions on a particular electrode interface we physically eradicated the cathode or anode from the electrolyte media prior to storage testing. As expected, hydrogen formation can be attributed to the reduction of water by the lithiated anode. Carbon monoxide appeared to be formed on the anode as well. Carbon dioxide was found to form on both electrodes.

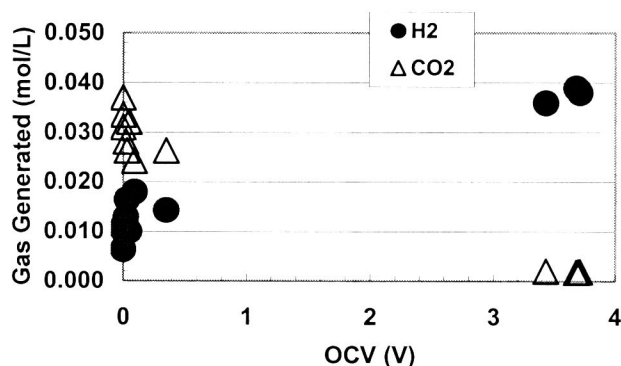
The effect of moisture, HF content, OCV and soluble catalytic species on gas evolution reactions will be discussed in detail and the encompassing reaction sequences will be proposed.

## REFERENCES

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4. H. Christoper, M. Brundage, L. Branovich, A. Pellegrino, S. Slane, T. Atwater, J. DeCarlo, P. Rodriguez, Proc. 37<sup>th</sup> Power Sources Conference, Cherry Hill, NJ, p. 342 (1996).



**Figure 1.** Effect of water injection on the gas generation. The cell was formed, charge to 20 % state of charge and left for storage at 20 – 25 °C under open circuit.



**Figure 2.** Composition of gas generated after 2-week storage at room temperature as a function of final OCV. Cells were charged to 20 % state of charge prior to storage and left under open circuit.

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