Electrolyte Production and Handling

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Abstract

The Grant Chemical Division of Ferro Corp. has been in the business of supplying commercial quantities of lithium battery Electrolyte solvents and solutions since 1976. Within the last 18 months we have endeavored to become expert in the handling of $LiPF_6$ and in the manufacture of $LiPF_6$ solutions.

We have been privileged to become the supplier of electrolyte solution to several recent lithium-ion battery start-ups. One of these is in Korea and that business is being handled by our exclusive agent here, SEMYUNG ENERGY.

Most primary battery formulations have some combination of the following solvents; monoglyme (DME) dioxolane, tetraglyme, gamma butyrolactone, ethylene carbonate (EC), propylene carbonate (PC). Most lithium-ion formulations contain a combination of EC, PC, dimethy carbonate (DMC), and diethyl carbonate (DEC). However, methyl ethyl carbonate (MEC) is popular and formate esters give low temperature properties. Lithium metal anode rechargeables can be formulated with any of the above solvents. MEC is interesting in that it gives such good low temperature properties and can be used in very high concentrations and still give very good cell performance. However, its value is tempered by recent evidence that during cycling of cells containing DMC and DEC, large concentrations of MEC build up. Also, MEC is very expensive and adds considerably to the cost of an electrolyte solution.

Salts used for primaries are $LiClO_4$, Li triflate, $LiBF_4$, and $LiAsF_6$. $LiPF_6$ dominates the lithium-ion systems, but the borate and arsenate are still of interest. 3M Corp. is promoting the use of two very interesting salts; the $LiN(triflate)_2$, and Li bis ethyl triflate imide (BETI). Both salts give interesting results in both primaries and secondaries, and should find markets for niche

applications, particularly where high temperature are encountered and where safety is a major consideration.

The supply of solvents and salts for lithium-ion batteries appears to be in good balance. However, all judgements of an adequate supply are to be strongly tempered by whether or not EV's are commercialized. If that happens, there will be a need to massively increase the supply of the basic solvents and salts. Ube Corp. in Japan seems to have enough capacity for good quality linear carbonates and Bayer Corp. and SNPE in Europe have considerable capacity for DEC and SNPE had DMC capability. Although these European supplies are based on phosgene chemistry and their products have chlorinated impurities, it appears possible to purify these materials to make acceptable solvent. More work is needed. Nisso in Japan makes most of the cyclic carbonates used in Japanese batteries, and BASF in Germany has some capacity to make crude cyclic carbonate. However, the world supply of these materials is dominated by Arco and Huntsman in the US. Huntsman recently started up a 23000 mt plant. That plant is mostly empty waiting mainly for the lithium-ion market to develop.

The supply of salts is certainly adequate for the near future. Hashimoto has a new 300 mt plant and Morita also has considerable capacity. Central Glass and Nisso Denko are also looking to be suppliers. In the US, ARC and Elf Atochem have produced development quantities and several other companies are looking to jump in. Although the characteristics that constitute a "good" solvent and a "good" salt for primary systems is extremely close to that for secondary systems, there are certain critical differences that we will discuss.

Most of the few differences have to do with odd chemical characteristics of the other cell components. For instance, glycol diethers (mainly DME) are a major component in almost all primary systems. However, they are not used in secondary systems for two reasons: one, their voltage decomposition level is a little lower than that of the carbonates, and two, they tend to solubilize the anode (particularly graphite) and cathode materials used in secondary systems. But, is it possible that some of the decomposition problems are related to impurities in the cathode material? Furthermore, will the advent of new anode materials (SnO_2) give a new lease to DME? Somewhat the same can be said for PC. It also has a slightly lower voltage decomposition potential than EC and it tends to attack graphite. However, it is used in some lithium-ion formulations and may well grow in popularity as battery chemists learn to control better their cell chemistry.

The basic purity requirements needed in a solvent to make a good lithium battery are:

1. Low water (very low for lithium-ion cells)
2. Low chloride
3. Very high over-all chemical purity

It appears that water levels in electrolytes for primary systems are not as important as believed by most battery chemists. However, water and hydroxyl groups are extremely important in secondaries since one molecule of water will generate two molecules of HF from the reaction with $LiPF_6$. In carbonate solution, essentially all the water that was trapped in the salt crystal and was in the solvent will be gone in 24 hours. The glycols take longer. It is interesting to note that battery manufacturing people are still specifying water levels in $LiPF_6$.

We do not know all the factors which affect color, HF levels and performance of lithium-ion battery electrolyte solution, It certainly appears that if one uses poor quality salt and solvent to make a solution and then use immediately to make a battery, that battery will have better performance characteristics than if the solution were stored a month then used to make the battery. The changing of the cell seems to stop electrolyte degradation. There seems to be several mechanisms of color formation. One of them does not seem to affect battery performance. These problems with poorly defined reasons put a burden on the manufacturer and shipper of solutions. It is obvious that more work is needed to better define the chemistries and role of trace impurities in $LiPF_6$-carbonate solutions.