NOVEL ELECTROLYTE ADDITIVES FOR OVER CHARGE PROTECTION AT LOW CURRENT

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Overcharge safety is one of the most critical safety requirements for lithium ion and lithium polymer batteries. One protection approach is to use integrated protection circuit and positive temperature coefficient (PCT) device; the second approach is to use electrolyte additives to make the cells inherently safe during overcharge abuse. Various electrolyte additives for overcharge protection of lithium batteries have been studied and developed over the last decade [1-7]. The additives prevent cell overcharge by either of the mechanisms: 1) Electro polymerization. This type of additives is represented by Moli developed biphenyl [1]. 2)Redox shuttle. Represented additive is fluorinated anisoles developed by Sony [4]. Polymerization additives normally function well in Li-ion batteries at high current overcharge, and redox shuttle additives are effective at low current overcharge and cell to cell balancing in multi-pack battery modules. Under overcharge conditions, unlike polymerization additives which will polymerized at cathode surface and the cell will no longer function, redox shuttle additives can keep the cell function.

In this paper, a new type of redox additives are presented. The detail structure of the additives will be disclosed after the patent application is accomplished. Figure 1 illustrates the coin cell test results for four additives, RDX231, RDX293, RDX 294 and RDX296 with 5% concentration in regular 1M $LiPF_6$ EC/DEC electrolyte. The coin cells were under constant charging current 0.1mA (~C/30 rate). It can be seen that without addition of the redox additives, the charging voltage of the blank control cell reached 5.0 volt relative quickly after cell reach 100% state of charge (4.20V). With addition of the redox additive, the shuttling voltages were kept steady for more than 100 hours after cell reached 100% state of charge. The shuttling voltages were in the range of 4.5 to 4.9 volt vs Li/L+.

After coin cell redox shuttle additive screening tests in coin cells, the additives were tested in full lithium polymer cells with 800mAhr capacity with $LiCoO_2/LiNiCoO_2$ cathodes and MCMB anodes. As shown in Figure 2, the addition of 1.5%wt of RDX293, RDX294 AND RDX296 showed cycle life around 350 to 380 cycles with 80% retained capacity. It is very close to that of blank control cell's 400 cycle life. In addition to cycle life tests, the effect of the redox additives on rate capability of the polymer cells were also tested and shown in Figure 3. It can be seen that the addition of the redox additives caused a slight decrease of rate capability. The 2C rate decreased from 97% to 95%, while 3C rate decreased from 93% to 87%. AC impedance tests demonstrated that the slight decrease of the rate capability by addition of the redox additives are due to increase of electrode impedance after the addition of the above additives. The effect of the redox additives on anode and cathode impedance growth will be further discussed and presented in the meeting.

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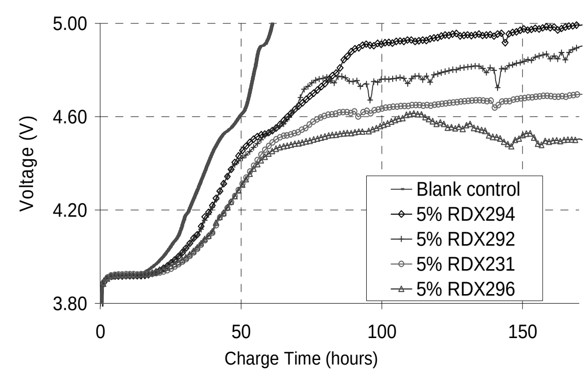

Figure 1. coin cell test results with 0.1mA charge current; Coin Cells Contain $LiCoO_2$ cathode, lithium metal anode and 1M $LiPF_6$ EC/DEC electrolyte with 5% wt additives.

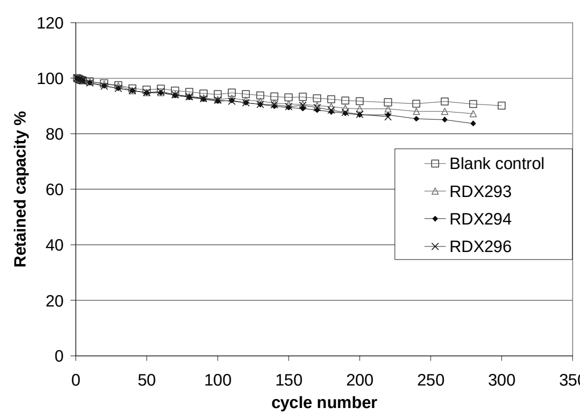

Figure 2. Room temperature cycle life for 800mAhr lithium polymer batteries. The batteries contained $LiCoO_2$ /$LiNiCoO_2$ cathode MCMB anode and 1M LiPF6 EC/DEC electrolyte with 1.5% wt redox additives.

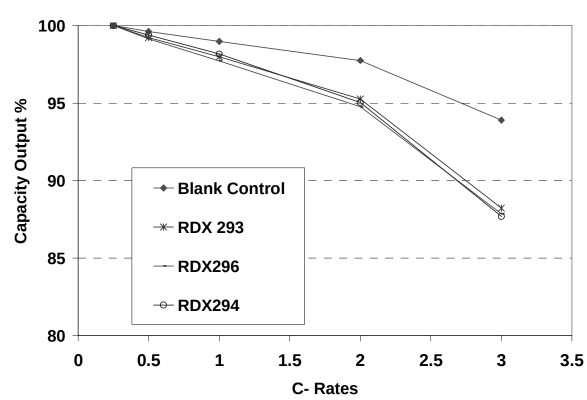

Figure 3. Rate capability of the 800mAhr polymer cells. The batteries contained $LiCoO_2$ /$LiNiCoO_2$ cathode MCMB anode and 1M LiPF6 EC/DEC electrolyte with 1.5% wt redox additives.

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