Layered $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ as Cathode for high Power and High energy Li-ion Batteries

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$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ could be an alternative cathode to $Li(Ni_{0.8}Co_{0.2})O_2$ and could offer longer calendar and cycle life for both HEV and high energy applications. The amount of active nickel in this material is small and the bulk oxidation of Ni to tetravalent state takes place at 4.6 V. In addition inactive Mn^{4+} cations in the structure play a stabilizing role preventing a structural collapse during cycling. By considering these two factors, we should expect no phase segregation in the case of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ system within the voltage window 3-4.2V which was one of the causes identified for power and capacity fade in the $Li(Ni_{0.8}Co_{0.2})O_2$ cathode. Also, this material can be made at a much lower cost and exhibits better safety characteristics than the $Li(Ni_{0.8}Co_{0.2})O_2$ material

Figure 1 shows the discharge performance of graphite/ $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell between C/25 to 10C rates at room temperature using a 1.2M $LiPF_6$/EC:PC:3DMC electrolyte. The cell shows excellent rate capability with limited capacity loss at 10 C full charge and discharge.

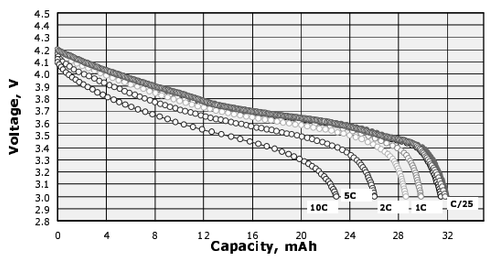

Fig.1 Discharge curve of graphite / $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell at room temperature.

Also, the graphite/ $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell cycled very well between 3.0 and 4.2V at about 1 C rate (See Fig 2). The capacity fade up to 100 cycles was negligible with a capacity retention of 99%.

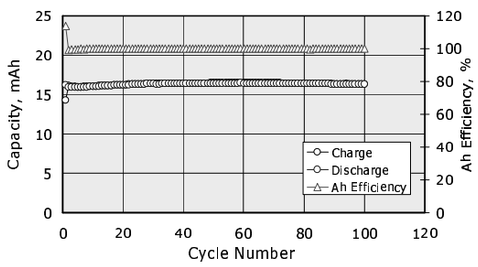

Fig. 2 Cycling result of graphite/ $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell at 1C rate and 25°C.

Figure 3 presents the TEM image of discharged $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ electrode after extensive cycling at 1C rate. The result mainly shows that $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ maintains its crystallinity and layered structure without any defect that might be caused by extensive cycling at such a high rate. The retention of the crystallinity of the $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ even at this very high rate full charge and discharge might be expected to expand the life of the battery based on this system. This result was corroborated by X-ray diffraction of a material from a cell that was cycled at 5C rate for 200 cycles. After this extensive cycling at such a high rate, the X-ray of the cathode material shows very sharp peak similar to those of the starting material. EDAX results also indicated that Ni, Co, and Mn were distributed in the structure in a homogeneous way.

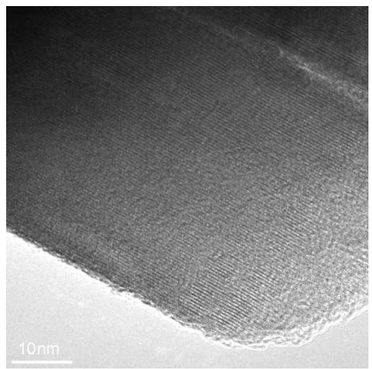

Fig.3 TEM image of $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ electrode after cycling.

Figure 4 presents the area specific impedance (ASI) for the 18-s pulse discharge and 2-s regenerative charge as a function of depth of discharge (DOD). The ASI's values are lower than those calculated by Argonne National Laboratory (ANL) battery design spreadsheet model for 25 kW battery packs, which are 35 $\Omega.cm^2$ for an 18-s discharge and 25 $\Omega.cm^2$ for a 2-s charge pulse. We found that this cell meets the power requirements especially in the "sweet spot" of 30-70% DOD. This result clearly indicates that a battery based on C/ $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell system meets and exceeds the power requirement for the HEV application.

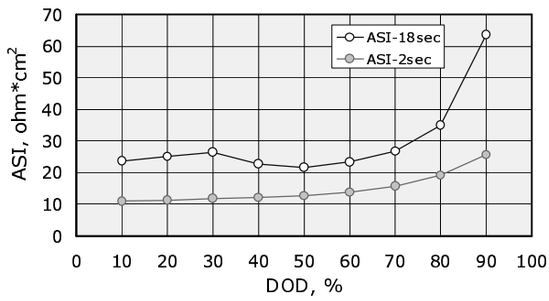

Fig.4 ASI of graphite/ $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell during hybrid pulse power characteristics test.

Preliminary accelerated calendar life testing shows that the impedance of the cell based on $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ is stable after 50 days of aging at 4.1V SOC and 50°C. This cathode material also has excellent safety characteristics with low reactivity with $LiPF_6$ based electrolytes at full charge. In this case, the material generate less heat than in the case of $Li(Ni_{0.8}Co_{0.2})O_2$ material . In addition, the onset temperature of most of the observed thermal peaks in the $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ were higher.

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References

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