

Short communication

Variation study for the fast charging lithium ion batteries

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Received 2 August 2006; received in revised form 20 December 2006; accepted 20 December 2006

Available online 9 January 2007

Abstract

Cell components in lithium ion cells have been studied to check their effects to reduce the charge time. Factors including various separator thickness, tab width, LiPF₆ concentration and solvent composition in electrolytes, cathode thickness, anode thickness and cathode active materials were studied. In addition, charge time of lithium ion cells was studied based on the charge voltage of cell. The most important variable in reducing the charge time of lithium ion cells was found to be the thickness of the cathode. The charge time of the lithium ion cells was reduced with thinner cathode. Other variables such as the separator thickness, LiPF₆ concentration and solvent composition in electrolytes, anode thickness and charge voltage of lithium ion cells were also effective in reducing the charge time of the cells, but with fewer impacts.

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Keywords: Lithium; Ion; Battery; Charge; Rate

1. Introduction

Lithium ion batteries are the major rechargeable power sources for portable electronic devices because of their high output voltage and high energy density. There has been an increase in demand for reducing the charging time of lithium ion batteries for the applications of power tools, electric vehicles (EVs/HEVs), portable electronics and military devices.

Rechargeable lithium ion batteries are composed of cathode [1–3], anode [4,5], separator, liquid electrolyte [6,7] or gel electrolyte [8,9] in metal case or plastic pouch. Transition metal oxides such as LiCoO₂, LiNiO₂ and LiNi_xM_{1-x}O₂ (M = metal or semimetal or transition metal or their mixture) have been thoroughly investigated as the cathode active materials. However, LiCoO₂ have been the dominant cathode active materials in commercial lithium ion batteries because of the technical issues related to LiNiO₂ or LiNi_xM_{1-x}O₂, such as the safety concerns and swelling issue during storage at over 60 °C. Graphite has been used predominantly as the anode active material among car-

bonaceous materials because of its high capacity, flat potential profile versus lithium and excellent cycle performance. Organic carbonate mixtures are commonly used as the solvents and lithium hexafluorophosphate (LiPF₆) as the salt for electrolyte, which has a high ionic conductivity and a wide electrochemical stability window [7]. Examples of gel-type electrolytes include a high ionic conductive gel polymer electrolyte [8]. The ionic conductivities of the ionic gel polymer electrolyte are very similar to that of a liquid electrolyte because the gel polymer electrolyte contains less than 2 wt.% of crosslinked ionic polymers, which can hold a large amount of polar solvents.

There have been some efforts to increase the rate performance and power density of lithium ion batteries by coating carbon black on LiCoO₂ cathode using surfactants [10] and by surface modification of graphite anode by zirconia [11]. However, these studies were focused on the discharge rate performance and the modification of the surface of active materials.

Most commercial lithium ion batteries have to be charged at low rates (0.5–1.0 C) and usually require 2–3 h of charge time. However, it is imperative to reduce charge time of lithium ion batteries for their commercial application for fast charging and high power applications. In this work, we attempted to investigate and identify the variables in reducing the charge time of lithium ion cells.

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Table 1
Charge time based on separator thickness

Separator thickness (μm)	25	20	16	12.5
Separator porosity (%)	55	41	<41	<41
Cell capacity (Ah)	2.6	2.6	2.6	2.6
Charge time (min)	72	77	73	68

2. Experimental

LiCoO₂ and graphite (MCMB) were used as cathode and anode active materials, respectively. The electrodes were purchased from SK Mobile Energy. Polyolefin microporous separators (Celgard Inc.) and lithium hexafluorophosphate (LiPF₆, Ferro Corporation) were used as received. Ethylene carbonate (EC, Ferro Corporation), diethyl carbonate (DEC, Ferro Corporation), ethylmethyl carbonate (EMC, Ferro Corporation), propylene carbonate (PC, Ferro Corporation), γ -butyrolactone (BL, Ferro Corporation), butyl acetate (BA, Aldrich) and propyl acetate (PA, Aldrich) were used without further purification. The cells were made by stacking process, in which electrodes were sandwiched in a Z-folded separator. Positive and negative leads were aluminum and nickel coated copper tabs respectively. The packaging material (Sumitomo) was aluminum laminate. All electrode assembly was conducted in the dry room (<1% humidity dry room). Ionic conductivities of electrolytes were measured by Oakton (CON5) and impedance of the cells was obtained by using Agilent 4338B. Cell performance was tested by using Arbin cyler at room temperature. Bar crush (width: 75 mm; thickness: 6 mm) and nail penetration (diameter of nail: 3.5 mm) tests were conducted in the crush and nail test chamber. Temperature of hot box test chamber was increased at 5 °C min⁻¹ to 150 °C and held at 150 °C for 10 min before it cooled down. Overcharge test of cell was conducted by using power supply (Hewlett Packard 6642A).

3. Results and discussion

The charge time of lithium ion cells has been studied by changing the separator thickness, tab width, salt concentration and solvent composition in electrolyte, cathode and anode thickness, cathode active materials, and the charge voltage.

Tables 1 and 2 show the charging time of lithium ion cells based on separate thickness and tab width, respectively. The thickness of separators were 25, 20, 16 and 12.5 μm . Tab widths were 4 and 10 mm. Lithium ion pouch cells were built with a typical capacity of 2.6 Ah at 0.2 C-rate for the study. Cathode (LiCoO₂) and anode (MCMB) loading in the cells were 19.2 and 9.2 mg cm⁻², respectively. Electrolyte contained 14 wt.% of LiPF₆ in a mixture carbonates solvent (EC/DEC/EMC = 30/30/40 wt.%). Cells were charged to 4.2 V

Table 2
Charge time based on tab width

Tab width (mm)	4	10
Separator thickness (μm)	20	20
Charge time (min)	77	78

at 3 C-rate (7.5 Amp) with a cut-off current of 0.05 C or 0.125 A. As we can see in Table 1, the cell with the thinnest separator (12.5 μm) had the shortest charge time among the cells and it took 68 min to be fully charged. The cell with the thickest separator (25 μm) took 72 min for the full charge, which is 4 min longer than that with the thinnest separator. However, cells employing 20 μm separator had the longest charge time (77 min) among the cells. On the other hand, the separator with 25 μm thickness had 55% of porosity while the separator with 20 μm thickness had a porosity of approximately 41%. This indicates that both the separator thickness and the porosity of separator impact the charge rate of lithium ion cells. In general, thinner separator has a lower porosity, which is easier for manufacturer to maintain the mechanical strength of the separator for battery applications. To improve the charge rate of the lithium ion cells, the separator should be thinner and its porosity should be higher.

As we can see on Table 2, tab width did not affect the charge time (77 min) of cells at the same charge condition at 3 C-rate (7.5 Amp).

Fig. 1 shows the ionic conductivity of electrolyte and the charge time of cells based on LiPF₆ concentration in the electrolyte. LiPF₆ concentration varied from 8 to 20% in the mixture carbonates solvents (EC/DEC/EMC = 30/30/40 wt.%). Cells were built with 12.5 μm of separators and the loading of cathode and anode were 15.4 and 7.4 mg cm⁻², respectively. Ionic conductivity of electrolyte peaked at 12 wt.% of LiPF₆ concentration and the electrolyte with 20 wt.% of LiPF₆ concentration had the lowest ionic conductivity among the electrolytes. The shortest charging time of the cell was approximately 47 min with the electrolyte containing 12 wt.% of lithium salts. In summary, when ionic conductivity of electrolyte was increased, charging time of the cell was reduced because higher ionic conductivity of electrolyte enhances the mobility of ionic species to result in increasing the charging rate of the cell.

Electrodes with various thicknesses were prepared to study the impact of electrode thickness on the charge time of lithium ion cells. Cathode thicknesses (active layer on aluminum foil) were 29.0, 34.5, 40.0, 46.0 and 51.5 μm . Anode thicknesses were 33.5, 40.0, 46.5, 53.5 and 59.5 μm . Fig. 2 shows the charge time

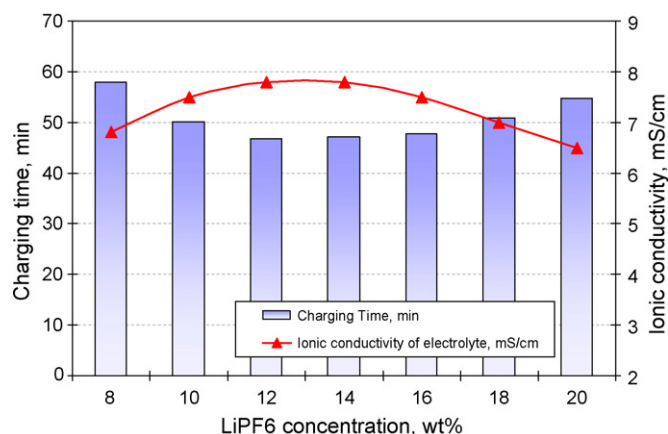


Fig. 1. Ionic conductivity of electrolyte and charge time of cells based on LiPF₆ concentration.

based on electrode thicknesses. Fig. 2(1) is the charging time of lithium ion cells as a function of cathode thicknesses in which anode loading was fixed at 8.6 mg cm^{-2} (thickness: $59.5 \text{ }\mu\text{m}$). Charge time was increased in proportion to the cathode thickness and had the shortest charge time (43.9 min) with the thinnest cathode thickness ($29.0 \text{ }\mu\text{m}$). This implicates that cathode thickness is extremely important for the high rate charge of the lithium ion cell. In general, cathode has approximately $10^{-2} \text{ S cm}^{-1}$ of electrical conductivity when it is not contaminated with non-aqueous electrolyte, an electrical insulator. It is almost one magnitude higher than the ionic conductivity of non-aqueous electrolyte, which has between 10^{-3} and $10^{-2} \text{ S cm}^{-1}$. However, the electrical conductivity of cathode can be reduced by the electrolyte penetration into the electrode after activation of the cell. In addition, the electrical conductivity of cathode is gradually reduced during the cycle. Thus, the low electrical conductivity of cathode is the most important variable in limiting the fast charging of lithium ion cells over the ionic conductivity of non-aqueous electrolyte. Fig. 2(2) shows the charging time as a function of anode thicknesses in which cathode loading was fixed at 10 mg cm^{-2} (thickness: $29.0 \text{ }\mu\text{m}$). The shortest charge time was achieved with the $40 \text{ }\mu\text{m}$ thickness anode instead of the thinnest anode ($33.5 \text{ }\mu\text{m}$). We found that the cell with the thinnest anode ($33.5 \text{ }\mu\text{m}$) had a lithium metal deposition on anode surface during the cycle while cells using thicker anodes

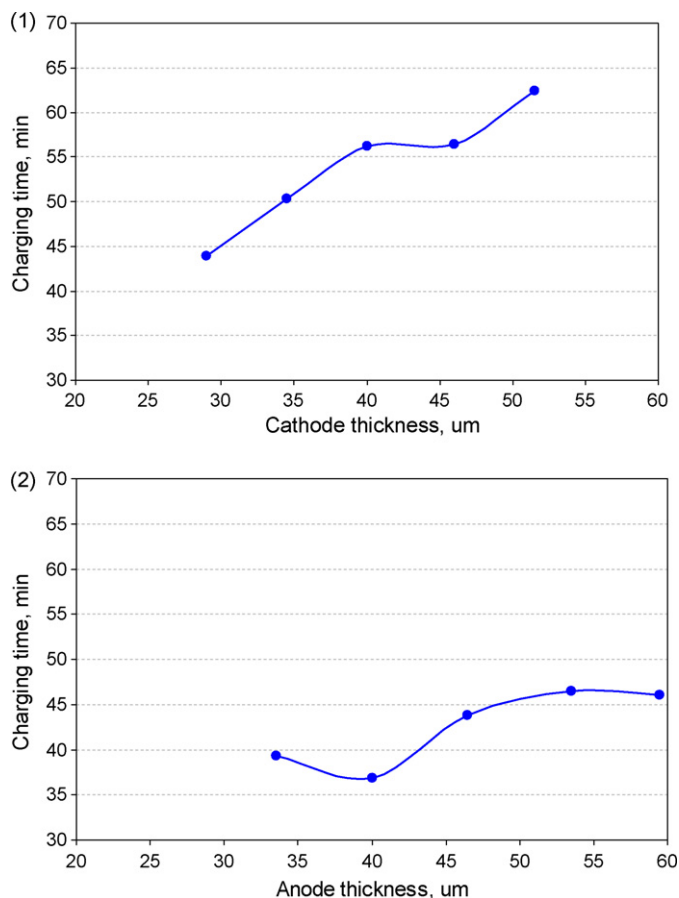


Fig. 2. Charge time based on electrode thickness. (1) Charge time vs. cathode thickness. (2) Charge time vs. anode thickness.

Table 3

Ionic conductivities of electrolytes based on solvent compositions

	Organic solvent compositions	Ionic conductivity (mS cm^{-1})
Electrolyte I	EC/DEC (40/60 wt.%)	6.5
Electrolyte II	EC/DEC (30/70 wt.%)	6.4
Electrolyte III	EC/DEC/EMC (30/30/40 wt.%)	7.4
Electrolyte IV	EC/DEC/PA (30/30/40 wt.%)	8.6
Electrolyte V	EC/DEC/BA (30/30/40 wt.%)	7.0
Electrolyte VI	EC/DEC/PC (30/30/40 wt.%)	5.9
Electrolyte VII	EC/DEC/BL (30/30/40 wt.%)	9.4
Electrolyte VIII	EC/EMC/BL (30/30/40 wt.%)	10.6

did not. This indicates that low electronically conducting lithium metal deposition on graphite anode also reduces the fast charging of the lithium ion cell. Thus, the extra amount of anode active materials were necessary to build lithium ion cells for reducing the charge time of cells to avoid lithium metal formation on graphite surface at high charge rate. Though the anode thickness affected for the charge time, it had limited impacts with the existing design. This indicates that the cathode thickness is more important than the anode thickness.

The charge rate of lithium ion cells has been studied based on different cathode active materials since cathode is very important to reduce charge time of the cells. Cells were produced by using $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and LiCoO_2 cathodes. For comparison, both cells had the same anode and same capacities (4.1 Ah). However, the cathode with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (capacity: $\sim 180 \text{ mAh g}^{-1}$) was 14% thinner than LiCoO_2 cathode (capacity: $\sim 145 \text{ mAh g}^{-1}$) because of its higher capacity. Cells were charged to 4.2 V at 3 C-rate (12.3 Amp) with a cut-off current of 0.05 C or 0.205 A. The cell with thinner $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ took 35 min to be fully charged while the other with LiCoO_2 took over 39 min.

Table 3 shows the ionic conductivity of electrolyte based on solvent compositions. All electrolytes contained 12 wt.% of LiPF_6 . The ionic conductivities of electrolytes were changed based on solvent compositions, and electrolyte VII and VIII containing BL had the highest ionic conductivities over 9 mS cm^{-1} .

Table 4 shows the impedance and charge time of cells based on solvent compositions. Capacities of cells at 0.2 C were approximately 3.8 Ah. Cells were built with $12.5 \text{ }\mu\text{m}$ separator and the thicknesses of cathode and anode were 34.5 and $40.0 \text{ }\mu\text{m}$, respectively. Cell VII and VIII having BL in the electrolytes had higher impedance and longer charge time than others, even though their electrolytes had higher ionic conductivities than

Table 4

Impedance and charge time of cells based on solvent compositions

Cell	Electrolyte	Impedance ($\text{m}\Omega$)	Charge time (min)
Cell I	Electrolyte I	6.7	38.6
Cell II	Electrolyte II	7.1	39.4
Cell III	Electrolyte III	6.7	34.2
Cell IV	Electrolyte IV	7.2	34.9
Cell V	Electrolyte V	6.8	35.2
Cell VI	Electrolyte VI	6.8	36.7
Cell VII	Electrolyte VII	8.7	40.3
Cell VIII	Electrolyte VIII	8.8	40.5

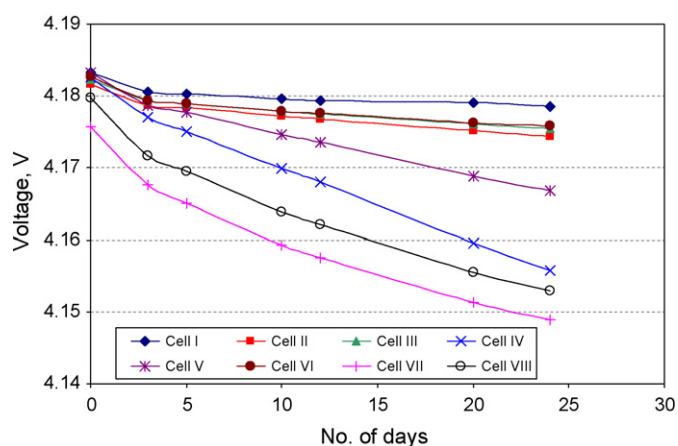


Fig. 3. Voltage drop of cells during RT storage based on solvent compositions.

others did. This is due to the fact that BL is not stable on the graphite anode, and generates a thick SEI layer on the electrode surface. The shortest charge time of lithium ion cells was obtained by the electrolyte containing PA (Electrolyte IV) or EMC (Electrolyte III), which had higher ionic conductivities than others excluding the electrolyte compositions containing BL. Their charge time was under 35 min.

Fig. 3 shows the voltage drop of fully charged cells containing the various solvents in the electrolytes during storage at room temperature. Cells were charged to 4.2 V at 1 C-rate (3.8 A) with a cut-off current of 0.05 C or 0.19 A. BL-containing Cell VII and VIII (bottom two lines) had the highest voltage drop during storage, and BA-containing cell IV and PA-containing cell V (center two lines) also had higher voltage drop than cell I, II, III and VI, which had a mixture of carbonates solvents. This indicates that solvent containing the ester group is not stable in lithium ion cells and causes the high self-discharge rate. The lowest voltage drop was obtained from cell I, which contains the highest amount of EC in the electrolyte. It is well known that EC has the uniform SEI forming capability on graphite based anodes [12], which results in lower self-discharge rate of lithium ion batteries. Our observations further confirmed their works.

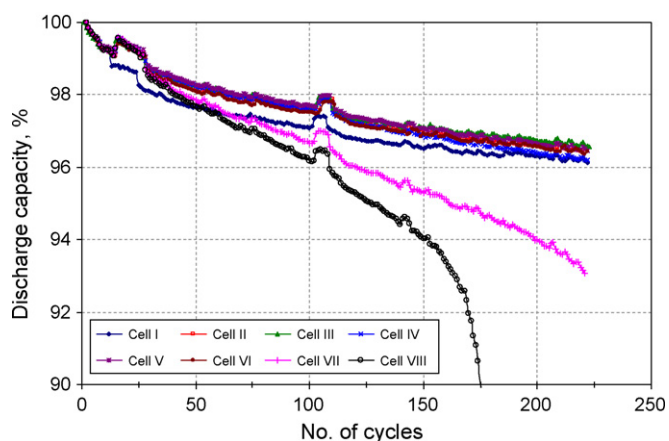


Fig. 4. Cycle performance of cells based on solvent compositions in the electrolyte.

Table 5
Charge time, impedance and capacity of cell based on charge voltage

Charge voltage (V)	Charge time (min)	Impedance (mΩ)	Capacity (Ah)	Capacity increase (%)
4.2	37.10	7.7	3.785	0
4.3	38.68	7.6	4.065	7.4
4.4	38.58	7.6	4.343	14.7
4.5	35.63	7.4	4.657	23.0

Fig. 4 shows the cycle performance of cells based on solvent compositions. Cells were charged at 0.5 C-rate (1.9 A) to 4.2 V with cut-off current at 0.19 A, and then discharged at 0.5 C-rate (1.9 A) to 3.0 V. The cycle performance of cells (except cells VII and VIII containing BL in the electrolyte) was very good and similar to one another. They had the capacity retention of approximately 96% after 225 cycles. Lithium ion cells containing the thinner electrodes have stronger adhesion between the active layer and the metal current collector, which results in limited impacts of the solvents compositions for the cycle performance of the cell.

Table 5 summarizes the charge time, impedance and capacity of cells based on the charge voltage of cells. Cells were built with 12.5 μm separator and the thickness of active layer on cathode and anode were 34.5 and 42.0 μm, respectively. Capacity of anode was approximately 20% higher than that of cathode in the cell for the study. Cells were charged from 4.2 to 4.5 V at 3 C-rate (11.4 Amp) with a cut-off current of 0.05 C-rate (0.19 A). Capacity of the cells was increased significantly when they were charged to higher voltage. Surprisingly, the shortest charge time of cell was achieved by charging it to 4.5 V instead of 4.2 V, which increases the cell capacity by approximately 23%. Although the higher voltage charged cell had slightly lower impedance than the lower voltage charged one, its impedance was not much different to explain the phenomena. Thus, we checked the maximum temperature of cell during the charge and found that the temperature of higher voltage (4.5 V) charged cell increased 13 °C while the lower voltage charged one increased 11 °C. This is because the higher voltage (4.5 V) charged cell has longer constant current charge mode at 3 C-rate than the lower voltage charged one due to its higher voltage charge. We also believe the temperature of the cell can be also effective in the charge rate of the cell.

Fig. 5 shows the cycle performance of cells charged to higher voltages of 4.3 and 4.5 V followed by discharge to 3.0 V at 1 C rate. They showed an excellent cycle performance regardless of the charge voltages. Capacity retention of both cells was approximately 96% after 300 cycles. This indicates that lithium ion cells containing LiCoO₂ could be charged to 4.5 V instead of 4.2 V without sacrificing their cycle performance if extra amount (>20%) of anode active material is used in the cell. However, cells charged at higher voltage have some disadvantages. First, the voltage drop of higher voltage charged cell is higher than nominal voltage charged cell to 4.2 V. Second, it sacrifices the safety of the cells. Tables 6 and 7 summarize the voltage drop of cells charged at higher voltage compared to nominal voltage charged cells and safety test results of the higher voltage charged

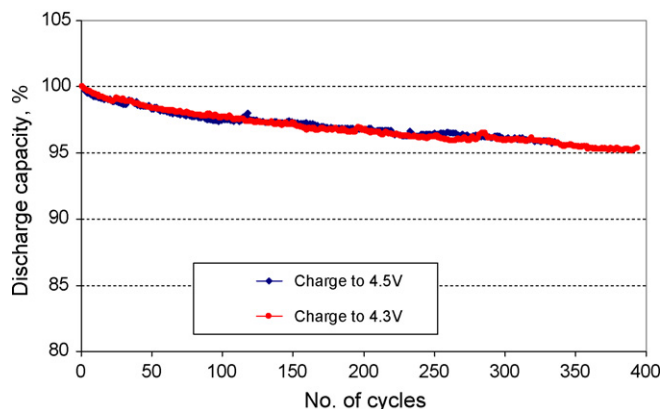


Fig. 5. Cycle performance of the cells charged to higher voltages.

Table 6
Voltage drop of cells during RT storage

Storage days (RT)	Cell charged to 4.5 V		Cell charged to 4.2 V	
	Voltage (V)	$\Delta V/\text{day}$ (mV)	Voltage (V)	$\Delta V/\text{day}$ (mV)
0	4.4895	–	4.1828	–
3	4.4751	~5	4.1802	~1
8	4.4666	~1	4.1785	~0.3
26	4.4562	~0.6	4.1741	~0.2

Table 7
Safety test results

Charge voltage (V)	Bar crush	Nail penetration	Hot box	Over-charge (4.6 V)
4.2	No smoke, no fire	Smoke, no fire	No smoke, no fire	No smoke, no fire
4.3	Smoke, no fire	Fire		
4.5	Fire	Fire		

cells. A cell charged at 4.5 V had approximately three times faster voltage drop than a cell charged at 4.2 V at fully charged state. In addition, higher voltage charged cell (4.5 V) failed during bar crush and nail penetration test, while the nominal voltage charged cell passed the safety tests. Lithium metal plating on anode could be developed from fast charging of lithium ion cells to reduce the self-discharge rate of the cell, enhance the side reaction with the electrolyte, and sacrifice to the overall safety of the cell.

4. Conclusions

Lithium ion pouch cells were produced and studied with various separator thickness, tab width, LiPF_6 concentration and

solvent composition, cathode thickness, anode thickness, cathode active materials and charge voltages.

Among the variables in this study, cathode thickness was the most important variable in reducing the charge time of lithium ion cells. Charge time was increased in proportion to the increase of cathode thicknesses because of its low electronic conductivity. Cells containing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ were charged faster than cells having LiCoO_2 at the same capacity range because the thickness of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode was thinner than LiCoO_2 cathode due to its higher capacity.

Thinner and more porous separator reduced the charge time slightly, while tab width was not effective in reducing the charge time of the 3.8 Ah cell. Optimization of solvent compositions and salt concentrations in the electrolyte are necessary to reduce the charge time. The shortest charging time of the cells was achieved by using the electrolyte containing 12 wt.% of lithium salts (LiPF_6) in EC/DEC/EMC mixture solvents.

Cells charged at higher voltage (4.5 V) had a shorter charge time than that charged at 4.2 V, and increased the cell capacity by >20%. Cells charged at higher voltages (4.3 and 4.5 V) also had good cycle performances if the anode was balanced correctly. However, it increased the self-discharge rate and sacrificed the safety of lithium ion cells due to the lithium metal formation on anode.

Acknowledgement

The authors gratefully acknowledge U.S. Army RDECOM for funding this work under the contract W15P7T-04-C-P016 and W15P7T-05-C-R009.

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