

LI-ION CELL DEVELOPMENT FOR LOW TEMPERATURE APPLICATIONS

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ABSTRACT

The results of electrode and the electrolyte studies at low temperatures (-40 °C) suggest that poor low temperature performance of Li-ion cells is limited by the carbon electrodes. It is suggested that the main causes for the poor low temperature Li-ion cell performance are: i) low Li-ion diffusivity in bulk carbon, ii) a Li-ion diffusivity in carbon that decreases with increasing Li composition and iii) limited Li capacity in carbon below -30 °C.

INTRODUCTION

Li-ion batteries⁽¹⁾ are widely used to power consumer products such as portable computers and cellular telephones. Their high specific energy and energy density, long cycle life, low self discharge and long shelf life make them highly desirable for defense and space applications also⁽²⁻³⁾. JPL/NASA is involved in the development of rechargeable Li-ion cells for future Mars Exploration Missions. The specific objectives are to improve the Li-ion cell cycle life performance and rate capability at low temperature in order to enhance survivability of the Mars lander and rover batteries. At present, it has been reported in the literature that the capacity of Li-ion cells at -40 C is 12% of the room temperature value⁽⁴⁾. To-date, it is believed that the performance of lithium-ion batteries at low temperatures is mainly limited by the electrolyte solution, which determines lithium-ion mobility between electrodes and also the transport properties of the passivation film on the anode. Most of the low temperature Li-ion cell studies have been focused on the development of low temperature electrolytes⁽⁴⁻⁸⁾, however, our studies on low temperature Li-ion cell performance have shown that the Li ion diffusion in carbon anode materials is actually controlling the low temperature cell performance. To identify the causes of poor low temperature Li-ion cell performance in order to further improve it in the future, we have evaluated the following: (1) low temperature electrolytes, (2) cathode performance, (3) anode performance, (4) Li diffusivity, (5) effect of electrode active

material particle size on cell low temperature performance, and (6) TiS_2 as an alternate anode. In this paper, we will discuss the results of our study.

EXPERIMENTAL

Experimental half and full cells were evaluated, at +20, -20, -30, and -40 °C, for: (1) charge/discharge characteristics, (2) faradaic utilization of the active material, (3) rate capability and (4) cycle life. The electrodes were made by spraying a solution containing an active material, polyvinylidene fluoride binder, and/or carbon black onto a metal foil substrate. The cells were activated with mixed solvent (such as Ethylene Carbonate (EC), Diethyl Carbonate (DEC), Dimethyl Carbonate (DMC), Ethyl Methyl Carbonate (EMC), and Propylene Carbonate (PC)) electrolytes containing LiPF_6 salt. Surface morphology and particle size of the electrode active material powders were examined using scanning electron microscopy.

RESULTS AND DISCUSSIONS

To identify compatible electrolytes for low temperature study, several combinations of organic solvents [(1) 1.0M LiPF_6 in EC:DEC:DMC (1:1:1), (2) 0.9M LiPF_6 in EC:DEC:DMC:PC (3:3:3:1), (3) 0.8M LiPF_6 in EC:DEC:DMC:EMC (3:5:4:1), and (4) 0.8M LiPF_6 in EC:DEC:DMC:EMC (3:5:4:2)] were mixed in different volumetric ratios and subsequently tested in transparent bottles placed in a low-temperature chamber. This preliminary test was used to visually determine, if the electrolyte froze or not at a given temperature. The electrolytes were kept at the following temperatures (-30, -35, -40, and -42.5 °C) for 4 days to give adequate time for freezing to occur. The results are listed for four different compositions in Table I. From Table I, it is apparent that the electrolyte #3 did not freeze at temperatures as low as -42.5 °C, thus, this electrolyte was selected for the -40 °C cell testing.

Table I. Determination of the electrolyte phases at various low temperatures

Label	Composition	-30°C	-35°C	-40°C	-42.5°C
1	EC:DEC:DMC (1:1:1) / 1.0M LiPF_6	Liquid	Liquid/Solid	Liquid/Solid	Solid
2	EC:DEC:DMC: PC (3:3:3:1) / 0.9M LiPF_6	Liquid	Liquid/Solid	Solid	Solid
3	EC:DEC:DMC: EMC (3:5:4:1) / 0.8M LiPF_6	Liquid	Liquid	Liquid	Liquid
4	EC:DEC:DMC: EMC (3:5:4:2) / 0.8M LiPF_6	Liquid	Liquid	Liquid/Solid	Liquid/Solid

In an attempt to identify the solvent component which solidified first with decreasing temperature, we conducted a test using the electrolyte with 1.0M LiPF₆ in EC:DEC:DMC (1:1:1). This electrolyte was kept at -40 °C for a week until it contained a liquid and solid mixture. The liquid and solid mixture was then separated and sealed in different containers. The analysis was performed using a Finnigan Incos XL Gas Chromatograph (GC)/Mass Spectrometer (MS). 0.1 µl of each sample was injected 'neat' into a 220 °C injection port with a split of ~1/50. The GC column used was a 30 meter DB-5 capillary column with 0.32 mm ID and 1µm film. The initial temperature was 30 °C for 4 minutes then ramped to 270 °C at 20 °C/min. The elution order of the three carbonate components was determined to be consistent with their boiling points, DMC first, DEC second, and EC last. Analysis of the solid precipitate was performed by first warming it up to melt it, then injecting it as a liquid. The analysis indicated the solid component was EC. Analysis of the supernatant liquid from which the solid precipitated appears to be higher in concentration in both DEC and DMC however, quantitative measurement is difficult due to inaccuracies in the injection mode and in response factors in the MS detector.

We have evaluated LiCo_{0.2}Ni_{0.8}O₂ cathode materials as well as the possibility of using carbon (coke or graphite) or TiS₂ as an anode material for low temperature applications. Some preliminary results of our half cell (Li/ LiCo_{0.2}Ni_{0.8}O₂; Li/coke; Li/graphite; Li/TiS₂) studies are listed below:

(1) Evaluation of cathode performance:

LiCo_{0.2}Ni_{0.8}O₂ material was evaluated for low temperature application. Fig. 1 shows LiCo_{0.2}Ni_{0.8}O₂ cathode utilizable capacity drops from 100% at +20 °C to 70%, 60%, and 46%, at -20, -30, and -40 °C, respectively. Our experimental data indicated that utilizable cathode capacity decreases rapidly below -30 °C due to the high polarization and slow Li diffusion. During the study, it was found that moderate rates for charging and discharging at -40 °C are not a problem for the cathode as shown in Fig. 2. In addition, at -30 °C, the same cathode could sustain initially a rate of C/25 for discharge for a short time period and then continued, during the same discharge process, at a higher discharge rate (C/8.3). Similarly for the charging processing, the cathode could be applied at initially a low rate charge (C/50) for a short time period, and then continued the charge process at a higher rate (C/16.6) (Fig. 3).

(2) Evaluation of anode performance:

(2A) Performance of graphite anode at low temperature: The low temperature electrochemical performance of Li intercalation and de-intercalation in Li/graphite half cells containing various electrolytes was studied. The half cells were charged at room temperature then, discharged at various low temperatures. Figure 4 shows the results of Li de-intercalation in cells containing 0.8M LiPF₆ in the EC:DEC:DMC:EMC (3:5:4:1) electrolyte at low temperatures. The de-intercalated Li capacities are 97.5% and 87% of room temperature (+20 °C) capacity for -30 and -40 °C testing, respectively. Figure 5 shows the results of Li de-intercalation out of graphite in

cells containing 1.0M LiPF₆ in the EC:DEC:DMC (1:1:1) electrolyte at low temperatures. The de-intercalation capacities are 100% and 84.6% of room temperature (+20 °C) capacity for -30 and -40 °C testing, respectively. From the above two examples, it appears that Li can easily be de-intercalated out of graphite at a reasonable rate (0.285 mA/cm²) at -40 °C, however, Li intercalation at the same rate, or even at a lower rate such as 0.0285 mA/cm² is very difficult at -40 °C. As described above, EC will precipitate out first when the temperature drops. However, from our studies for Li/graphite half cells containing electrolytes without EC, slow Li intercalation was still apparent. In addition, we have conducted cycle testing of Li-ion cells from RT to -40 °C and also from -40 °C to RT. These test cells consisting of graphite anodes and the low temperature electrolyte [0.8M LiPF₆ in EC:DEC:DMC:EMC (3:5:4:1)] were tested at room temperature (RT), -20 °C, -30 °C, and -40 °C. The waiting period after each temperature change was four days. The test result (Fig. 6) showed that the cell can function at -40 °C at very low charge/discharge currents. The capacity of the cells at -20 °C was > 80% of that at RT but at -30 °C only 35% of that at RT. From this result, it can be seen that there is a fundamental problem which reduces cell capacity that occurs in the temperature range -20 °C to -30 °C.

(2B) Measurement of Li-ion diffusivity in coke: Coke may have higher Li diffusivity than graphite at low temperature and hence, it is important to determine how lithium diffusion kinetics change with temperature in coke-based carbon anode materials. We have conducted an experiment using the Galvanostatic Intermittent Titration Technique (GITT) to measure Li diffusivity at various temperatures (+20, -20, -30, -40 °C). This technique consists of applying a small constant current to the cell at the equilibrium open circuit condition, and then monitoring the electrode potential change with time due to the change of surface concentration of electroactive species at the electrode and electrolyte interface. Our finding is that the room temperature Li-ion diffusivity in the coke material studied is 1.14×10^{-9} cm²/sec, however, the Li diffusivity declines to 1.38×10^{-10} , 6.64×10^{-11} , and 3.04×10^{-11} cm²/sec at -20, -30, and -40 °C, respectively (Fig. 7). The calculated activation energy for Li-ion diffusion in coke at low temperature is 0.384 (eV/atom) or 37 (KJ/mole).

(2C) Effect of coke particle size: For this study, the effect of coke particle on cell performance was investigated. We have evaluated the performance at various low temperatures of two coke anode materials having a different particle size (6 and 25 micron). A number of cells were fabricated and tested at room temperature (+20 °C) as well as at low temperatures (-20 °C, -30 °C) to determine their performance. The result showed that the cell having a coke anode containing the smaller particle size yields the better low temperature cycling performance (Fig. 8). The first cycle irreversible and reversible capacities of the two coke materials are in the range of 80 and 200 mAh/g, respectively. The coke material with the smaller particle size can be a future candidate anode material for low temperature Li-ion cell application.

(2D) Pseudo-coulometric titration curves: Half cells (Li/coke; Li/graphite) were fabricated and cycled for five formation cycles at room temperature. Both the coke and graphite electrodes have the same physical dimensions and similar weight for the active carbon materials. The first cycle charge and discharge profiles of the coke and graphite cells are compared in Fig. 9. These cells were then kept in a low temperature chamber at -40 °C for low temperature coulometric

titration studies to determine the thermodynamic Li capacities of coke and graphite. In the case of the coke anode, the results showed that about 87.7% of the room temperature lithium capacity (obtained @ $I = 0.285 \text{ (mA/cm}^2\text{)}$) was retained at $-40 \text{ }^\circ\text{C}$ (charge rate $=0.00095 \text{ (mA/cm}^2\text{)}$) (Fig. 10). The graphite anode, on the other hand, delivered 76.8% of its RT Li capacity under the same current density at $-40 \text{ }^\circ\text{C}$ (Fig. 11). The corresponding half cell potential (vs. Li) of 12% of its Li capacity is under 10 mV at the extremely low current condition. In addition, a two order of magnitude decrease in Li diffusivity for coke at $-40 \text{ }^\circ\text{C}$ compared to room temperature was determined by GITT analysis. By combining all the test results, the comparison of coke and graphite performance at LT can be summarized by the following: (a) Both coke and graphite have the similar Li capacity at $-40 \text{ }^\circ\text{C}$, (b) The lower voltage plateau of graphite is not usable, probably due to the slow Li diffusion in this compositional range. Actually, Li diffusivity in carbon decreases as the amount of Li in carbon increases. A similar trend is observed for coke in the last portion of the titration curve, and (c) The poor performance of carbon materials at low temperature is due to the slow Li diffusion at low temperature.

(2E) TiS_2 anodes for low temperature Li-ion cells: The performance of rechargeable Li-ion cells containing carbon anodes are limited by high polarization at the carbon electrode surface. Recently, we have demonstrated, in lab test cells, that the use of titanium disulfide (TiS_2) as an alternate anode material for low temperature use, can deliver high capacity, have high rate capabilities, and excellent capacity retention during cycling. TiS_2 material has a high Li diffusivity ($10^{-7} \text{ cm}^2\text{/sec}$) at room temperature. The low temperature performance of Li/ TiS_2 and Li/carbon half cells were evaluated and compared. Half cells containing carbon and TiS_2 electrodes and Li counter/reference electrodes were assembled and electrochemically tested first at room temperature and then at -30 and $-40 \text{ }^\circ\text{C}$. The electrochemical test results are shown in Figure 12. Figure 12 shows the voltage vs. capacity curves for Li-deintercalation from TiS_2 and graphite at different rates and temperatures. From Figure 12, it is apparent that at room temperature using a current density of 0.4 mA/cm^2 , graphite has a higher specific capacity than TiS_2 , 310 mAh/g and 205 mAh/g , respectively. However, at $-30 \text{ }^\circ\text{C}$, TiS_2 has a higher specific capacity than graphite, 150 mAh/g and 80 mAh/g , respectively. It is important to note that the current density used for TiS_2 at $-30 \text{ }^\circ\text{C}$ is 10 times higher than that used for graphite at $-30 \text{ }^\circ\text{C}$, 0.4 mA/cm^2 and 0.04 mA/cm^2 , respectively. Furthermore, as the temperature is decreased to $-40 \text{ }^\circ\text{C}$, TiS_2 can deliver 80 mAh/g using a current density of 0.4 mA/cm^2 , while graphite delivers only 17 mAh/g using a current density of 0.4 mA/cm^2 . To determine the cycling performance of TiS_2 anodes at low temperatures, half-cells were cycled at -30 and $-40 \text{ }^\circ\text{C}$. The results are plotted in Figure 13. In Figure 13, the charge capacity and temperature are plotted versus the cycle number. From Figure 13, it is apparent that the charge capacity (Li-deintercalation from TiS_2) at $-40 \text{ }^\circ\text{C}$ increases initially with cycling and later stabilizes at 130 (mAh/g) using a current density of $0.2 \text{ (mA/cm}^2\text{)}$.

CONCLUSIONS

In summary, the low temperature performance of $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ cathode and carbon anode were compared in this work. The results showed that the $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ cathode can be cycled at moderate charge and discharge rates at $-40\text{ }^\circ\text{C}$. The carbon anode, on the other hand, had very limited rate capability at $-40\text{ }^\circ\text{C}$. The performance degradation begins at $< -20\text{ }^\circ\text{C}$, however, if the carbon anode is charged at room temperature then it is easy for Li to be extracted at low temperature. Clearly, both the electrolyte and SEI do not inhibit de-intercalation. The low temperature performance of Li-ion cells is limited by the Li diffusion in carbon anode. The liquid organic electrolytes and the solid electrolyte interphase (SEI) are not responsible for the poor low temperature Li-ion cell performance. The fact that TiS_2 can deliver reasonably high specific capacity at high current densities at low temperatures ($\ll -20\text{ }^\circ\text{C}$) is due to its high Li diffusivity ($10^{-7}\text{ cm}^2/\text{sec}$). In general, coke has higher Li diffusivity than that of graphite. In the case of coke anode, a two order of magnitude decrease in Li diffusivity was determined by GITT when the temperature changes from $+20\text{ }^\circ\text{C}$ to $-40\text{ }^\circ\text{C}$. The main causes for the poor low temperature Li-ion cell performance are three fold: (a) slow Li-ion diffusion in the carbon bulk at low temperature, (b) Li-ion diffusivity decreases with the increasing in Li composition in carbon and (c) carbon has limited Li capacities below $-30\text{ }^\circ\text{C}$. In view of the experimental results, it is predicted that any further improvement in either electrolyte type, composition and conductivity will result in limited performance improvement of the Li-ion cell at $-40\text{ }^\circ\text{C}$ and hence, a novel anode material must be developed in order to improve both capacity and rate capability at $-40\text{ }^\circ\text{C}$.

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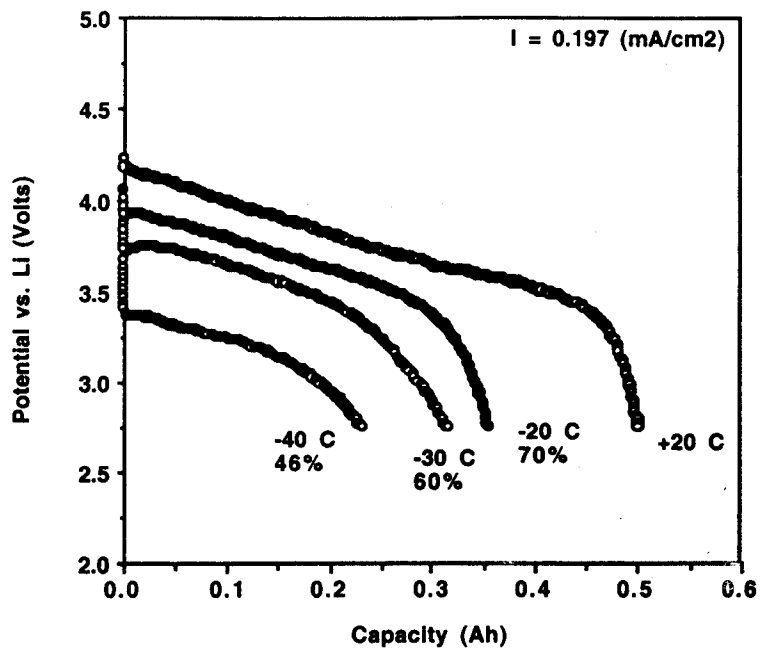


Figure 1. Evaluation of utilizable capacity for $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ cathode material at room temperature and various low temperatures.

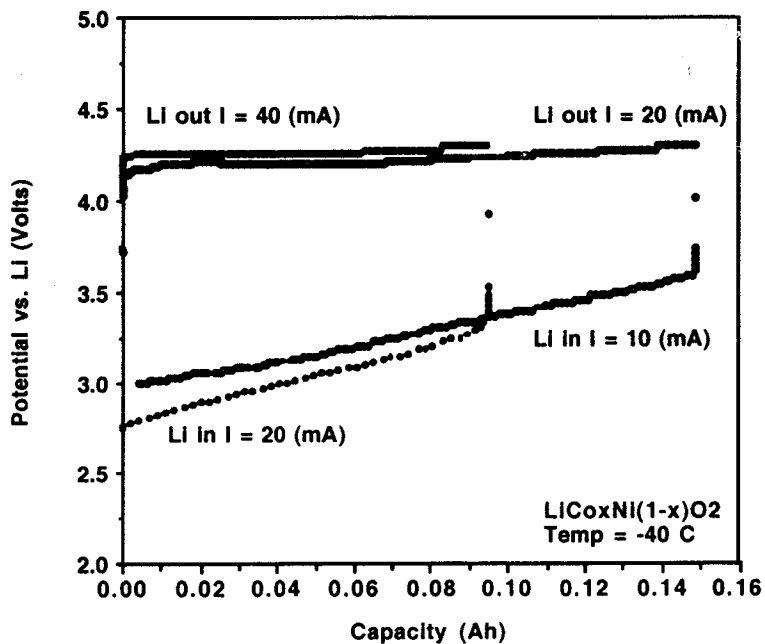


Figure 2. Charge and discharge profiles of $\text{Li/LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ cells at -40 C .

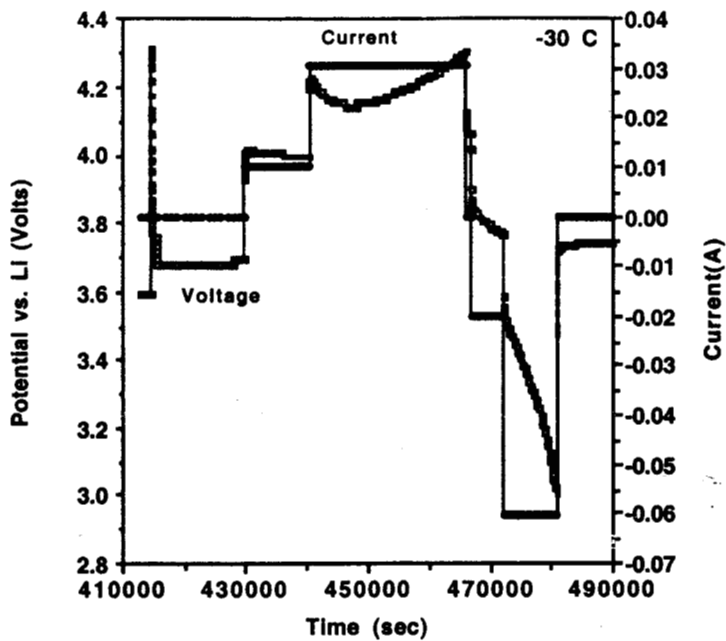


Figure 3. $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ cathode could be charged or discharged at initially a low rate for a short time period, and then continued the process at a higher rate.

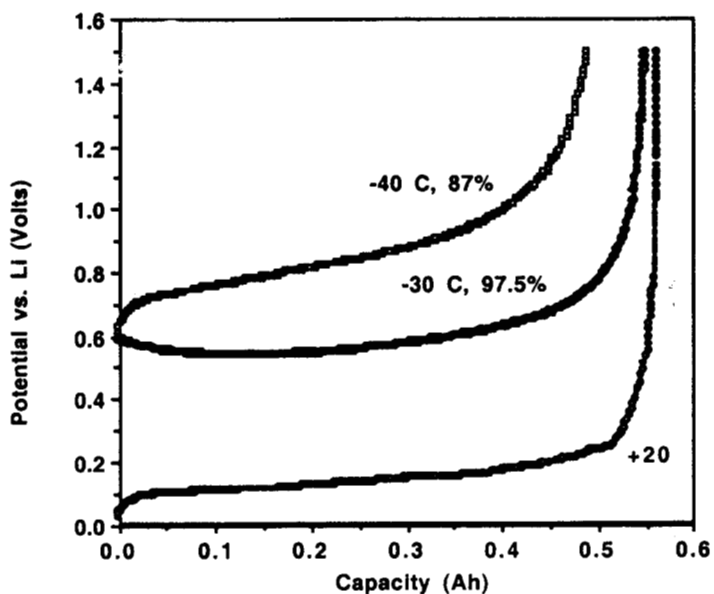


Figure 4. Li de-intercalation in cells containing 0.8M LiPF_6 in EC:DEC:DMC:EMC (3:5:4:1) electrolyte at low temperatures.

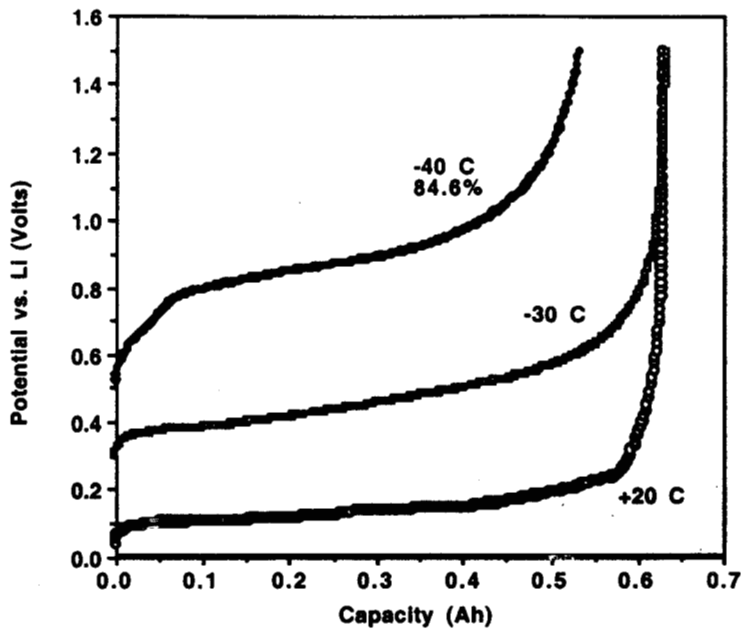


Figure 5. Li de-intercalation out of graphite in cells containing 1.0M LiPF_6 in EC:DEC:DMC (1:1:1) electrolyte at low temperatures.

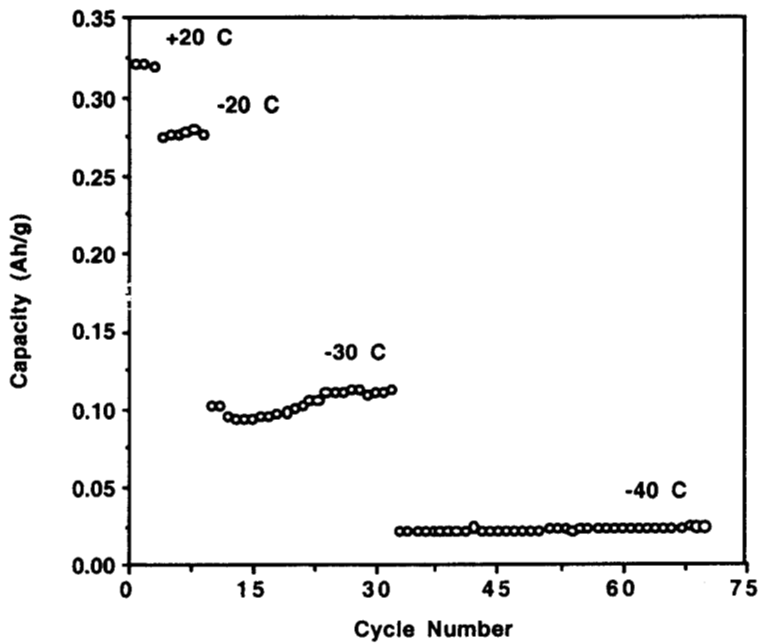


Figure 6. The Li/graphite cell can be cycled at -40°C at low charge/discharge currents.

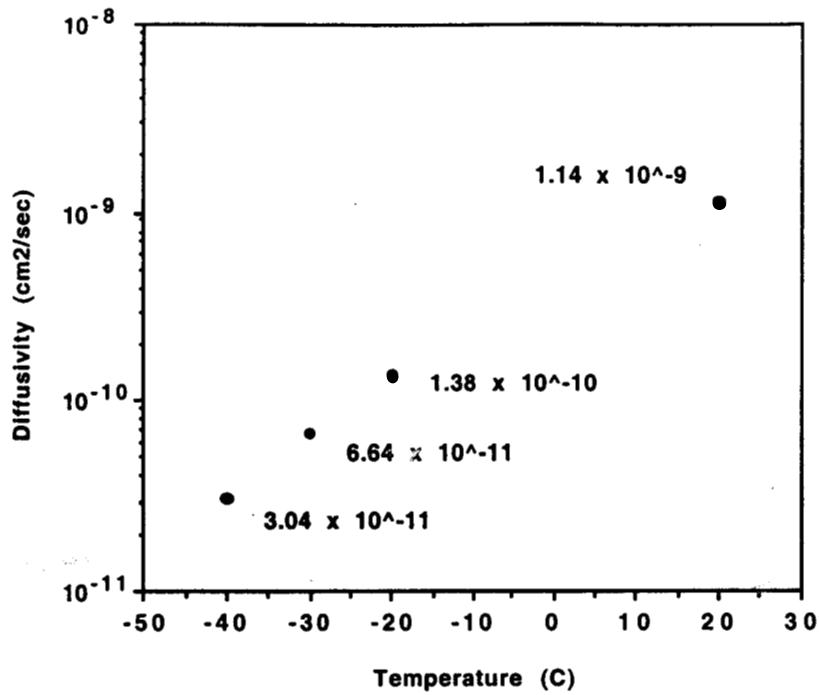


Figure 7. Li diffusivity in coke material measured by the Galvanostatic Intermittent Titration Technique (GITT).

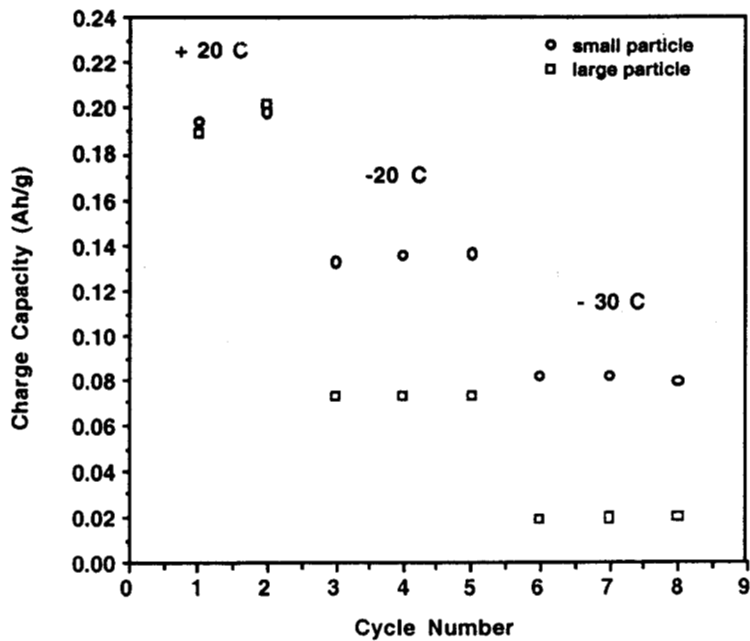


Figure 8. Effect of carbon particle size on the cell low temperature performance.

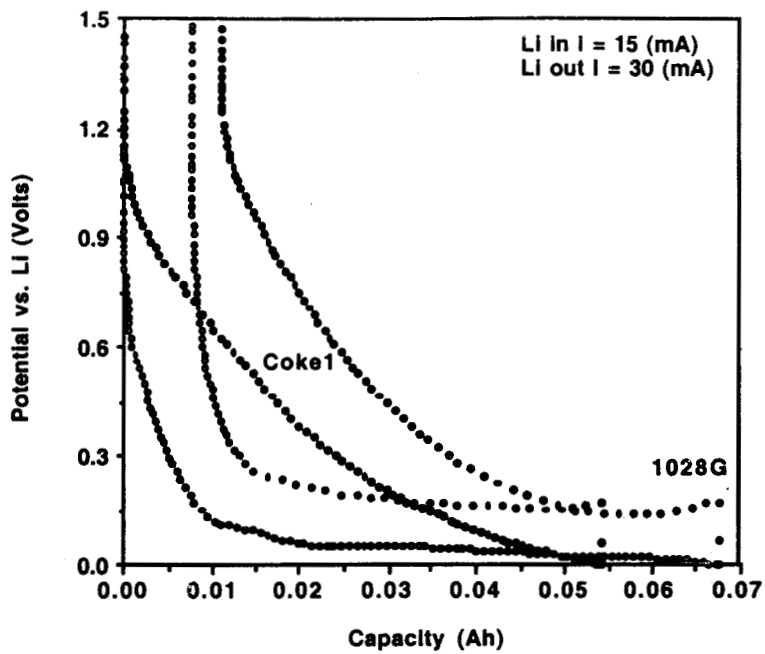


Figure 9. Comparison of the first cycle charge and discharge profiles of coke and graphite.

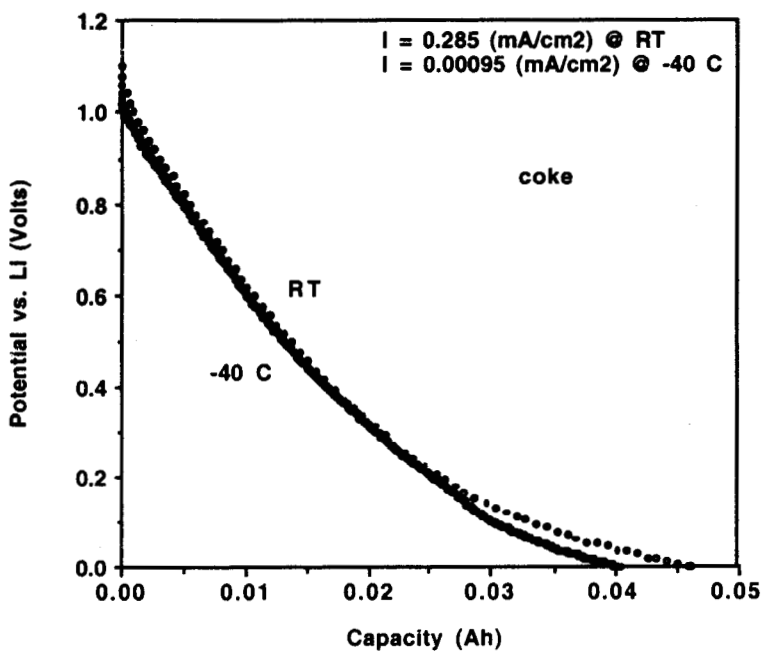


Figure 10. Comparison of the discharge profiles of Li/coke cell at room temperature (0.285 mA/cm²) and -40 °C (0.00095 mA/cm²).

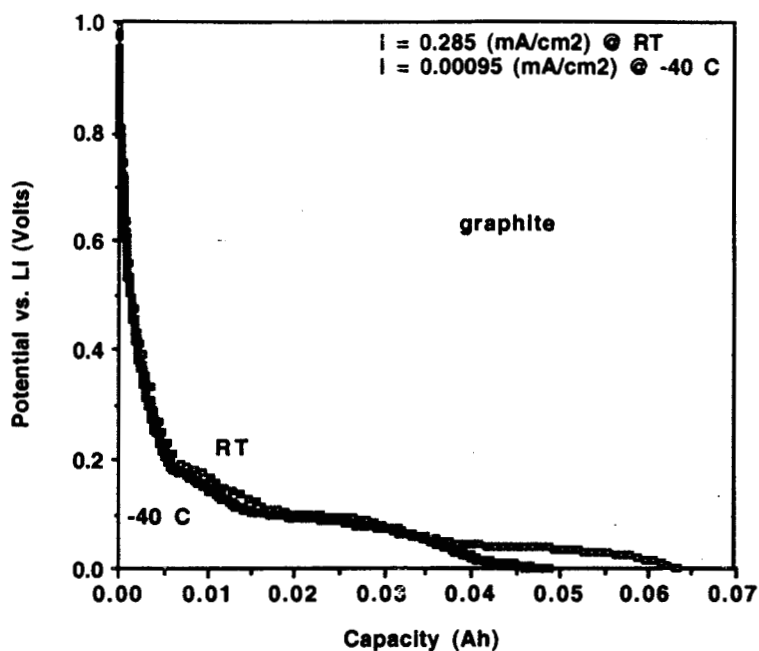


Figure 11. Comparison of the discharge profiles of Li/graphite cell at room temperature (0.285 mA/cm^2) and $-40 \text{ }^\circ\text{C}$ (0.00095 mA/cm^2).

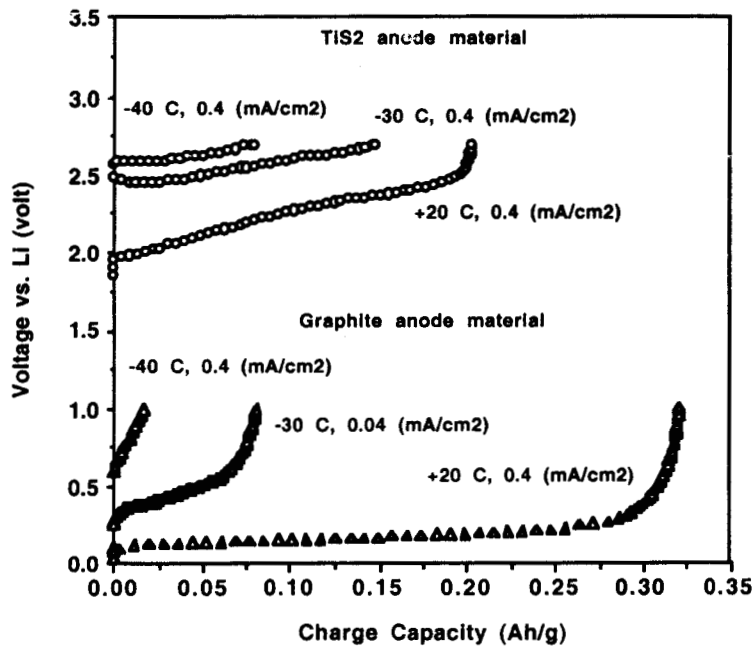


Figure 12. Voltage vs. capacity curves for Li de-intercalation from TiS_2 and graphite at different rates and temperatures.

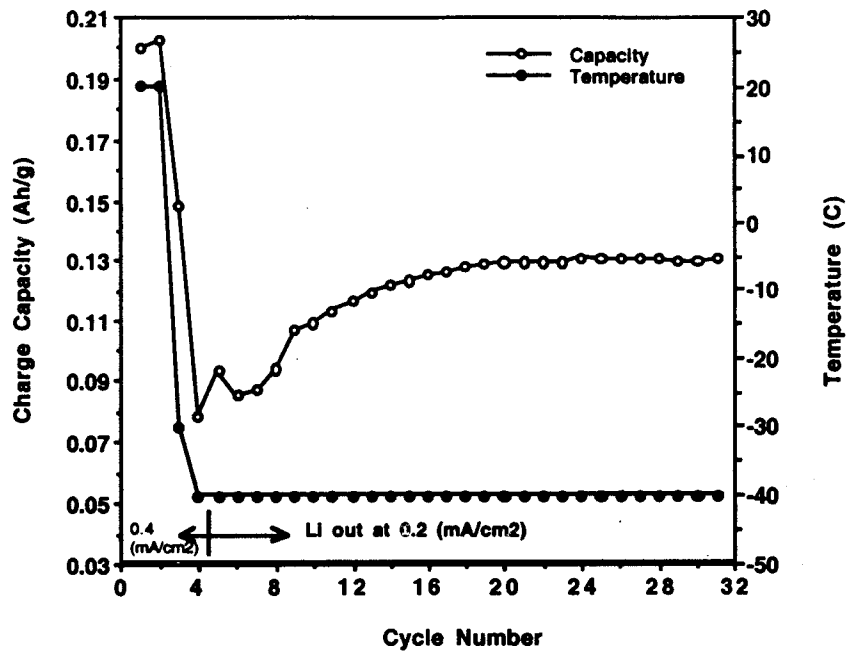


Figure 13. The cycling performance of Li/TiS₂ cell at room temperature and various low temperatures.