Nano Si/G composite anode in Li ion battery for aerospace applications

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A composite anode material with a composition of graphite-nano-silicon-ceramic-PEO+LiClO$_4$ has been investigated for Li ion batteries, and its performance at different temperatures (from -40°C to 45°C) and current densities analyzed using various electrochemical methods. Electrochemical behavior of composite anodes with different Si and ceramic compositions has been studied using galvanostatic charge-discharge cycling and AC impedance analysis. Composite anode with a composition of graphite (50%)-nano Si (10%)-ceramic (20%)-PEO+LiClO4 (20%) (Wt %) shows a stable reversible capacity of 300 mAh/g over 50 cycles at room temperature and a reversible capacity of 160 mAh/g at -30°C. Enhanced low temperature performance has been observed due to the addition of ceramic, which in turn increases the Li ion conductivity of the anode resulting in improved charge transfer kinetics.

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At room temperature, Li ion batteries exhibit high specific energy and energy density, long cycle life, and low self-discharge. Due to these properties, Li ion batteries are widely used in portable electronic devices. However, at temperatures below -20°C, commercial 18650 Li-ion battery exhibits very low specific capacity compared to the room temperature capacity[1,2], and hence does not satisfy the requirements for aerospace applications. The main reasons for poor low temperature performance are: (i) reduced ionic conductivity of the electrolyte, and solid electrolyte interface (SEI) film, (ii) limited Li ion diffusion ability in the anode, and (iii) increased charge transfer resistance leading to poor electrochemical kinetics. To improve the low-temperature conductivity of electrolytes, various electrolytes for Li ion batteries have been prepared and tested in the temperature range of 0°C to -40°C (refs 3-7). It was found that certain electrolytes with propylene carbonate[3] (PC), ethyl acetate[5] (EA), methyl butyrate[5] (MB), etc. as solvents show better low temperature performance as compared to commercial Li ion cell electrolytes. More detailed analysis by Huang et al.[8] and Li et al.[9] have shown that the ionic conductivities of the electrolyte and SEI film have less effect on low temperature performance as compared to charge transfer kinetics in the anode. This was also confirmed by AC impedance analysis[10,11]. From these results, it may be inferred that the low temperature performance can be improved by increasing the Li ion conductivity of the anode. This in turn, increases the Li ion diffusivity and reduces the charge transfer resistance.

Improving the specific capacity of the anode is another important issue for Li ion batteries. Among the group IV elements, silicon has high theoretical capacity of 4200 mAh/g (10 times > that of graphite) and it can also reversibly alloy with Li. However, Si exhibits 300% volume expansion during charge-discharge cycling process[12-14]. This generates enormous stress in the anode, leading to anode decrepitation and hence resulting in severe capacity fade[13,14]. Reducing the Si particle size to nano meters can only reduce the pulverization to a certain extent, but cannot suppress it completely. One way to overcome this problem is to embed the nano Si particles in a solid electronic conducting matrix. Various groups such as Yang et al.[15], Kim et al.[16], Liu et al.[17], and Kim et al.[18] have prepared Si/C composite anodes by pyrolysis of Si and carbon precursor materials, which showed a stable reversible capacity of 700mAh/g over 30 cycles. Wang et al.[19] reported a reversible capacity of 900mAh/g for Si/MCMB composite anode prepared from high energy mechanical milling. However, long cycling performance and low temperature performance for these anodes have not been reported.

To meet the NASA requirements for aerospace applications, anode for Li ion battery should have high specific capacity, good cycle life in the

temperature range of 60°C to -30°C and also the ability to be used in solid polymer electrolyte cells. In this paper, a new Si/graphite composite anode with high low-temperature performance is discussed. To improve the low temperature performance, ceramic powder with high Li ionic conductivity and low activation energy was mixed with nano Si-graphite composite. To further improve the low temperature performance, a suitable Li ion conductive polymer binder was chosen for preparation of the anode. The influence of ceramic on the low temperature performance has also been investigated.

Materials and Methods
Electrode preparation

Polyethylene oxide (Aldrich) and $LiClO_4$ (Aldrich) powders in 8.5:1.5 weight ratios were dissolved in acetonitrile (Sigma-Aldrich, 99.8%) to form a homogenous polymer solution. Lithium sulfide (Aldrich) and phosphorous pentasulfide (Aldrich) powders in 8:2 molar ratios were ball milled for 12h and then heat treated at 300°C for 2h to form a high Li-ion conductive ceramic powder. Graphite ks-4 (Timcal Group, Switzerland), Si, $80Li_2S\cdot20P_2S_5$ powder, and $(PEO)_{16}(LiClO_4)$-acetonitrile solution with different compositions were mixed and sealed in a stainless steel vial inside the argon-filled glove box. Mixing $80Li_2S\cdot20P_2S_5$ powder with G-Si-PEO composite anode increases the ionic conductivity of the anode, and also enhances low-temperature performance of the anode. Ceramic powder with a composition $80Li_2S\cdot20P_2S_5$ has a high room temperature conductivity of 7.2×10^{-4} S/cm and a low activation energy $(<0.3eV)^{20}$. Li ion conductive $LiClO_4$-PEO polymer was used as a binder to further improve the ionic conductivity of composite anode.

Using a SPEX-8000 high energy mechanical mill, the graphite-nano-Si-ceramics-PEO-LiClO₄ composite was mechanically milled for 5 min. to obtain a homogeneous slurry. The slurry was then rolled 4-5 times to form a high density Si/G composite thin film ($50\mu m$). This composite film was later used to couple with solid electrolyte. It has been observed that liquid electrolytes can hardly penetrate into high-density thin film (anode). Therefore, the Li ion mobility is highly dependent on Li ion conductive ceramics and PEO-LiCLO₄ in the anode. If high performance can be obtained from this anode using a liquid electrolyte, similar performance can also be obtained from the same anode using a solid electrolyte. It may be noted that solid electrolytes

have lower Li ion conductivity compared to liquid electrolytes. To investigate the influence of Si particle size on the electrochemical performance of the anodes, nano Si (30-70nm, Nanostructured & Amorphous Materials Inc) and micro Si (1-20μm, Aldrich) were used for the preparation of the anodes. To remove excess acetonitrile solvent, thin films were dried in a vacuum oven maintained at 100°C. Then, these dry thin films were pressed to enhance the contact between the active materials and the conductive graphite.

Electrochemical testing

The CR2032 coin cells, consisting of Si/G composite anode as the working electrode, a Li metal as a counter electrode, and $1M$ $LiPF_6$/EC/DEC/DMC/EMC (1:1:1:1:3 by vol., Ferro Corporation) as electrolyte, were assembled inside the glove box. $LiPF_6$/EC/DEC/DMC/EMC can be used as an electrolyte even at a temperature below -30°C. This is because of the existence of liquid phase even at a low temperature of -40°C (ref. 8). All the cells were galvanostatically discharged (Li insertion) and charged (Li extraction) in the range of 0-1.5V at different current densities using Arbin battery tester (model BT2000). Impedance analysis of all the anodes in half cells was done using a frequency response analyzer, (Solatran, FRA 1260) and an electrochemical interface (Solatran, model 1286). Before impedance measurements were made, all the anodes were discharged to 0 V and were maintained at 0 V for more than 3h. This process allowed the Li ions to be fully inserted into the anode. The ac impedance of the cell was measured, while maintaining a DC potential of 10mV over the frequency range of 1000 kHz – 0.001Hz.

Results and Discussion
Influence of Si particle size on electrochemical performance

Figure 1 shows the discharge charge capacities of micro and nano Si anodes for 37 cycles. These cells were discharged and charged at a current density of 20mA/g. During the initial cycle, nano Si anode showed a discharge capacity of 829mAh/g, and a charge capacity of 560mAh/g. This resulted in an irreversible capacity of 47.8%. Also, micro Si anode exhibited a discharge capacity of 789 mAh/g and a charge capacity of 573 mAh/g, resulting in irreversible capacity of 37.8%. Both these anodes showed an initial charge capacity which is nearly equivalent to the theoretical capacity (606 mAh/g), but the nano Si anode showed high irreversible
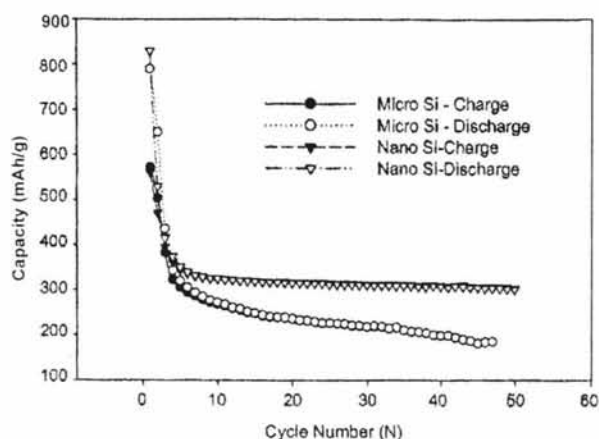
Fig. 1 – Galvanostatic cycling results for micro and nano Si anodes for 47 cycles. [Anode comp.: Graphite ks-4 (40%) – Si (10%) – ceramic (20%) – PEO- LiClO$_4$ (20%)].

Fig. 2 – Discharge-charge capacities for anodes with different Si content. [Anode comp.: Graphite ks-4 (60-x %) –nano Si (x%) – ceramic (20%) – PEO-LiClO$_4$ (20%) (x=10,15,20,25). Black dotted circles: Graphite ks-4 (60 %) – nano Si (10%) – ceramic (20%) – PVDF (10%)].

capacity. This can be attributed to the excess SEI film formation (resulting from high surface area of the nano Si particles compared to micro Si particles). Both these anodes showed severe capacity fade during the initial 5 cycles. After the 5th cycle, nano Si anode retained 61% of the initial charge capacity while the micro Si anode retained only 53%. After 47 cycles, the micro Si anode exhibited a charge capacity of 185 mAh/g, which is 32% of the initial charge capacity, while the nano Si anode showed 306 mAh/g charge capacity, which is 54% of the initial capacity. These results show better cyclability and capacity of the nano Si anode. Enhanced performance of the nano Si anodes is due to short diffusion lengths and lower pulverization of nano Si particles during charge/discharge. During the Li insertion and extraction process, large volume expansion and contraction takes place. This results in lattice distortion and further leads to enhancement of strain. The large strain will cause the particle to decrepitate, resulting in inter-particle disconnection. Hence, the active material is lost, finally leading to severe capacity loss. In nano Si particles, the diffusion lengths are short and this reduces relaxation times and further causes the material to be uniformly strained[21].

Influence of nano Si content on electrochemical performance

Electrodes with different nano Si compositions were prepared to determine the effect of nano Si content on cycling performance. Figure 2 shows the cycling performance of nano Si 10%, 15%, 20% and 25% anodes at 20mA/g current density. Among all the electrodes, nano Si 15% and 20% electrodes showed similar initial charge capacity of 770 mAh/g.
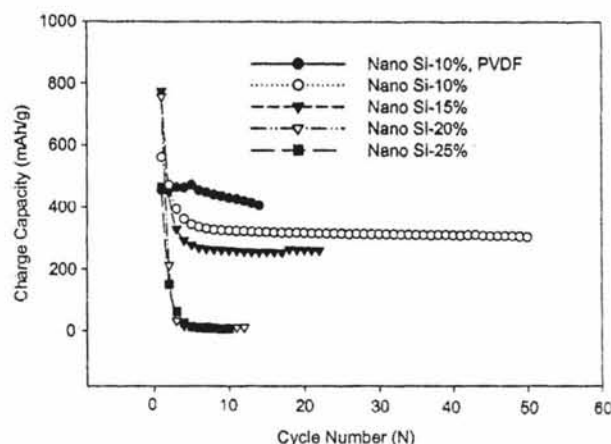
However, as the nano Si content in the anode increased, the initial irreversible capacity increased as well. Anode with composition nano Si 25% showed the highest irreversible capacity of 926mAh/g, and anode with nano Si 10% showed lowest irreversible capacity of 267mAh/g. As mentioned above, this is due to excess SEI film formation which results from high nano Si content. Higher nano Si content also resulted in degradation of cycling performance. Anode with nano Si 10% showed a stable reversible capacity of 302 mAh/g for 50 cycles, and anode with nano Si 15% showed a stable reversible capacity of 260 mAh/g for 22 cycles. Anodes with nano Si 20% and 25% exhibited poor cycle life of 7 cycles. This may be attributed to the spallation of nano Si particles from the thin film, which is caused by large volume expansion. It may be inferred that PEO-LiClO$_4$ polymer binder is not strong enough to accommodate the volume changes during Li insertion and extraction cycles. To validate this, the microstructure of nano Si 15% anode was examined using SEM analysis. After 12 cycles, the nano Si 15% anode film was taken out and dried at 80°C in a vacuum oven and then SEM micrographs were taken which are shown in Fig. 3. It can be seen that a number of holes (Fig. 3a) and cracks (Fig. 3b) were formed on the surface and resulting in uneven surface. These holes and cracks may be formed due to either (i) some of the electrode constituents being soluble in electrolyte or (ii) loss of nano Si particles during the cycling. To validate the reason under (i), solubility tests were carried out and it was found that none of the anode constituents was soluble in electrolyte. This indicates that the uneven
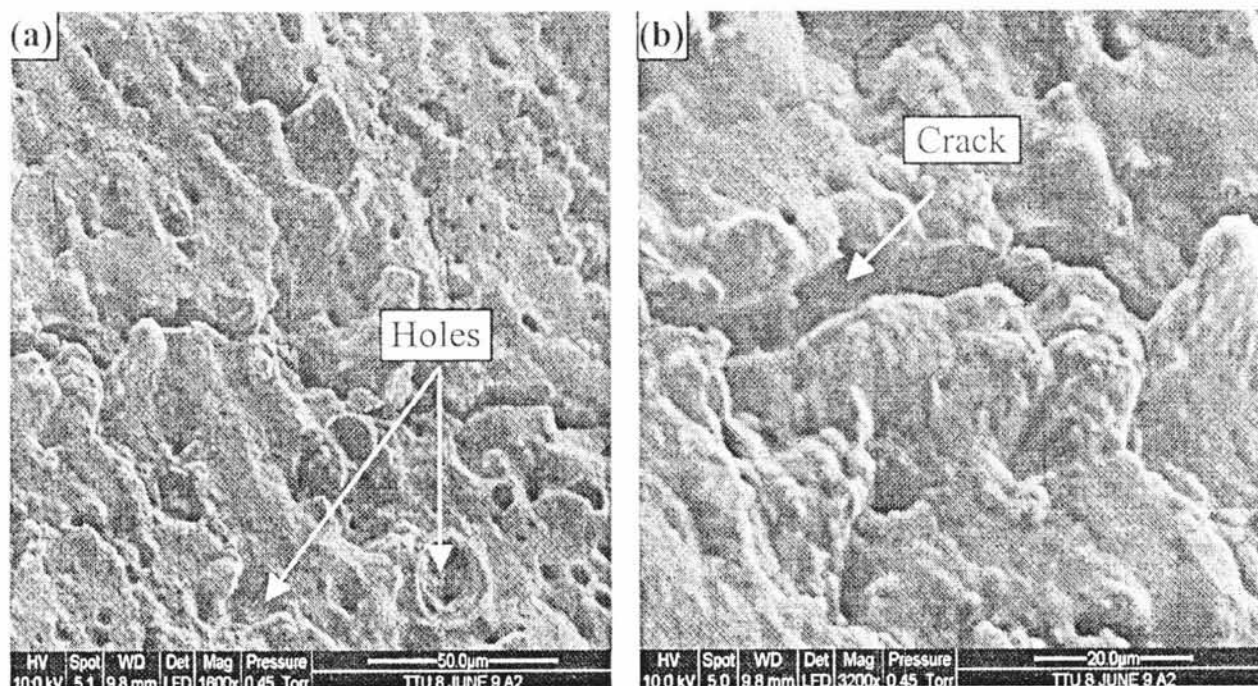
Fig. 3 – SEM images of nano Si 15% anode surface at (a) lower magnification and (b) higher magnification.

surface was formed due to the loss of nano Si particles. As mentioned above, during cycling, Si expansion and contraction takes place. During this process, the polymer binder strands are highly stretched, and these might break if the stress on these strands exceeds the breaking strain[22]. Hence these Si particles may become isolated and therefore the electrical contact will be lost. This ultimately results in loss of active Si. These isolated nano Si particles cannot be charged or discharged which results in capacity loss. This was also confirmed by microanalysis. Nano Si composition obtained from microanalysis was very low as compared to the nano Si composition used (15%). This justifies the reason under (ii). To validate the reason under (ii), a nano Si 10% anode using PVDF as binder was prepared and its electrochemical performance was tested, which is also shown in Fig 2. Though this anode showed a smaller initial charge capacity (454 mAh/g), it exhibited higher capacity retention (88%) compared to nano Si 10% anode, which showed 56% capacity retention after 14 cycles. The better capacity retention shown by nano Si 10%-PVDF anodes proves the inability of the PEO-LiClO$_4$ binder to accommodate the volume change during initial cycles. Further testing is in progress to determine the cycling performance and low temperature performance of nano Si 10%-PVDF anode and the results will be reported later.
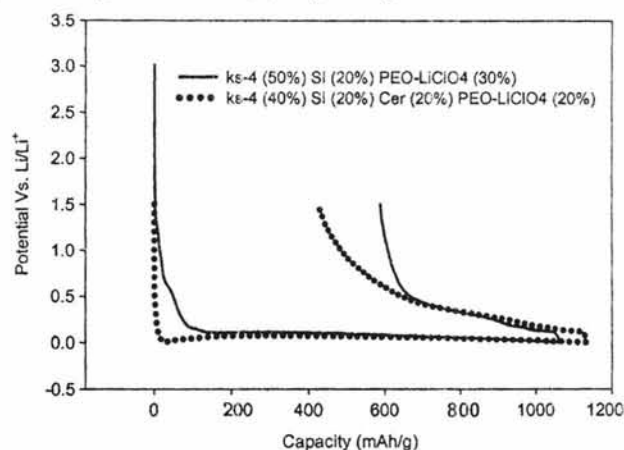

Fig. 4 – Voltage versus initial capacity curves for nano Si 20% anode with and without ceramic content.

Influence of ceramic addition on initial charge-discharge performance of 20% nano-Si composite anodes at room temperature

To determine the effect of ceramic powder on room temperature performance, two nano Si 20% anodes with and without ceramic content were prepared and the electrochemical performance was tested. Voltage vs. initial capacity curves for these two anodes are shown in Fig. 4. At 20 mAh/g current density, nano Si 20% anode without ceramic content showed an initial discharge capacity of 1058 mAh/g, a charge capacity of 470 mAh/g and an irreversible capacity of 124%. On addition of 20% ceramic, this anode showed an initial discharge capacity of 1132 mAh/g, a charge
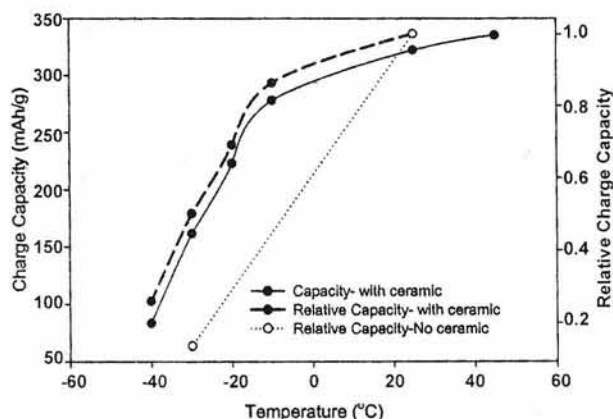
Fig. 5 – Charge capacity and relative capacities of Graphite ks-4 (50%) –nano Si (10%) – ceramic (20%) – PEO-LiClO₄ (20%) and Graphite ks-4 (60%) – nano Si (10%) – PEO-LiClO₄ (30%) anodes as a function of temperature.

Fig. 6 – Typical EIS of the Li ion half cell and the equivalent circuit used to fit the electron impedance study.

capacity of 707 mAh/g, and an irreversible capacity of 60%. From these results it is evident that addition of ceramic increased the initial charge-discharge capacities, and reduced the irreversible capacities. This is mainly due to high Li ion conductivity of the ceramic powder, which enhanced the Li insertion/extraction kinetics of composite anodes.

Influence of ceramic addition on charge-discharge performance of 10% nano-Si composite anodes in the temperature range of +45°C to – 40°C

Since $80Li_2S \cdot 20P_2S_5$ ceramic has a high room temperature Li-ion conductivity and low activation energy, the addition of ceramic into graphite-nano silicon composite anode may not only improve the kinetics at room temperature performance but also improve the kinetics at low- and high-temperatures. Due to better room temperature performance of nano Si 10% anode amongst all the anodes (Fig. 2), this anode was considered for low temperature performance testing. Two nano Si 10% anodes with and without ceramic content were prepared, galvanostatically discharged and charged at 5 mA/g current density in the temperature range of 45°C to -40°C. To facilitate the comparison of low temperature performance of these two anodes, a ratio of charge capacity at specific temperature to the charge capacity obtained at 25°C was defined as relative charge capacity. Figure 5 shows the relative charge capacities and charge capacities of the two anodes as a function of temperature. At 25°C, nano Si 10% ceramic 20% anode showed a charge capacity of 321 mAh/g. A slightly higher charge capacity (335 mAh/g) was obtained, when the temperature was increased to 45°C. This is due to increased
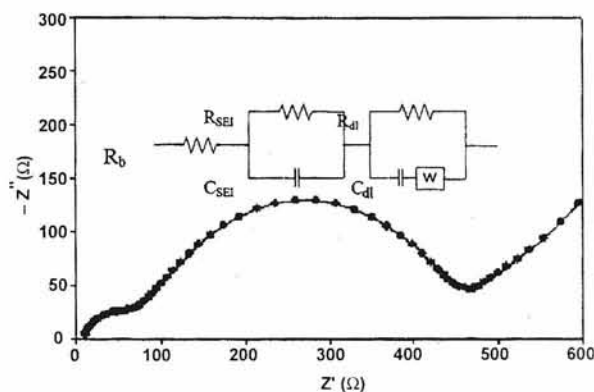
electrochemical reaction rate at high temperatures. When the temperatures were lowered to -10°C and -20°C, this anode exhibited higher charge capacities of 277 mAh/g and 222 mAh/g respectively and relative charge capacities of 0.86 and 0.69 respectively. A rapid decrease in capacity was observed when the temperature dropped below -20°C (Fig. 5). At -30°C and -40°C, nano Si 10% ceramic 20% anode exhibited charge capacities of 160 mAh/g and 84 mAh/g respectively and relative capacities of 0.5 and 0.2 respectively. However, at -30°C nano Si 10% anode without ceramic content showed a relative capacity of only 0.13, which is much lower than that of anode with ceramic addition.

Electrochemical impedance study (EIS)

To determine the reason for rapid decrease in capacity with temperature, EIS analysis for these two cells were carried out in the temperature range from 45°C to -40°C. Since the size of lithium foil counter electrode is much larger than the working (composite) electrode, impedance of G-nano Si-ceramic/lithium cell is mainly dependent on the composite electrodes. A typical Nyquist plot of Li ion half cells is shown in Fig. 6. From Fig. 6 it can be seen that impedance spectra of Li ion cell mainly consist of two partially overlapped semi circles and one sloping line. This kind of impedance spectra can be explained by drawing an equivalent circuit, which is also shown in Fig. 6. In Fig. 6, R_b represents the serial resistance, which includes resistances of electrolyte, separator, and electrodes. R_{SEI} (1st semi circle) and R_{ct} (2nd semi circle) represent the resistance of solid electrolyte interface film and charge transfer respectively. C_{SEI} and C_{dl} are the capacitance of SEI film and double layer respectively. W is the Warburg impedance related to Li ion diffusivity on the interface between
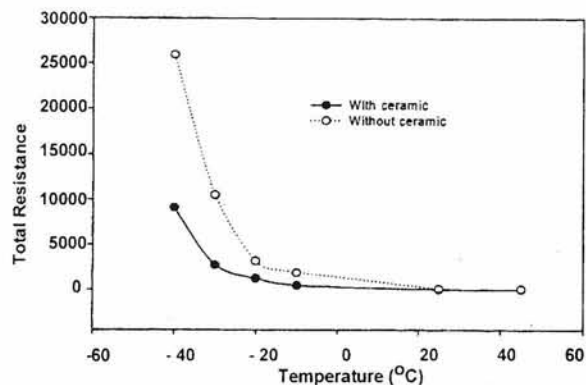
Fig. 7a – Temperature dependence of total resistance of Graphite ks-4 (50%) – nano Si (10%) – ceramic (20%) – PEO-LiClO$_4$ (20%) and Graphite ks-4 (60%) – nano Si (10%) – PEO-LiClO$_4$ (30%) anodes.
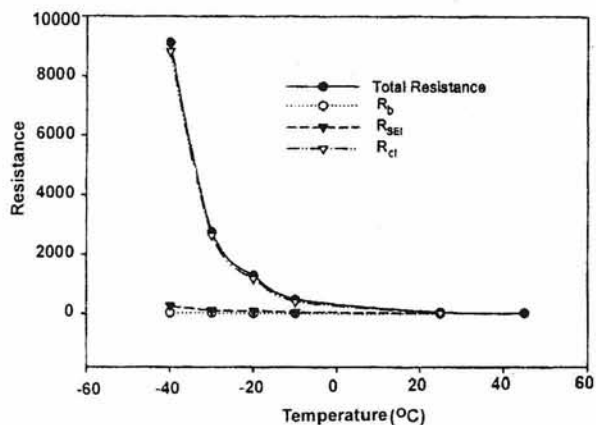

Fig. 7b – Temperature dependence of various resistances of Graphite ks-4 (50%) – nano Si (10%) – ceramic (20%) – PEO-LiClO$_4$ (20%) anode.
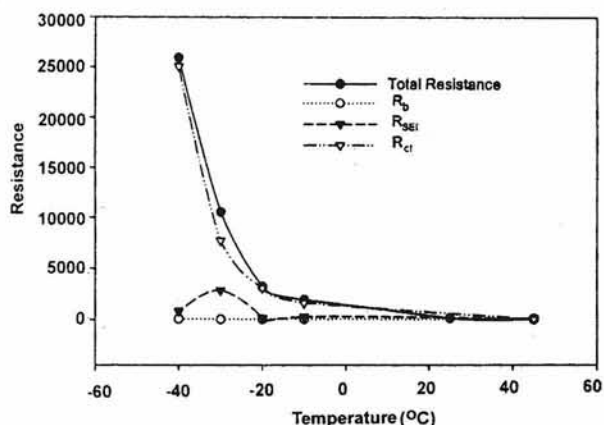

Fig. 7c – Temperature dependence of various resistances of Graphite ks-4 (60%) – nano Si (10%) – PEO-LiClO$_4$ (30%) anode.

the active materials and electrolyte, which is indicated by a straight sloping line. R_{ct} and W when combined together is called Faradic impedance which denotes the electrochemical kinetics of the cell[8]. Higher R_{ct} of the cell means lower kinetics of faradic reaction. Total resistance of the cell can be obtained by adding these three resistances.

From Nyquist plots obtained from EIS analysis, values of R_b, R_{SEI} and R_{ct} are obtained using an in-built program provided by Z-view software. Values of these resistances for nano Si 10% anode with and without ceramic content are plotted as a function of temperature (Figs 7a - 7c). Figure 7a shows the total resistance of the two cells as a function of temperature. From the graph it is evident that irrespective of the ceramic addition, the total resistance of the anode increased by a large percentage when the temperature is below -20°C. This explains the reason for the sudden decrease in charge capacity at -30°C for nano Si 10% anode with ceramic content (Fig. 5). At room temperature, no significant difference is observed in resistance for these two cells. But when the temperature is below 0°C, nano Si 10% anode without ceramic content showed higher resistance than that of nano Si 10% anode with ceramic addition. At -30°C and -40°C, addition of ceramic to nano Si 10% anode reduced the overall resistance four folds, which resulted in a high relative capacity of nano Si 10% - ceramic 20% anode compared to nano Si 10% - ceramic 0% anode (Fig. 5). To determine the influence of electrolyte, SEI and electrochemical reaction kinetics in determining the low temperature performance, individual resistances and total resistance of the two cells were plotted (Figs 7b and 7c, respectively). From Figs 7b and 7c, it is clear that total impedance of the cells is dominated by charge transfer resistance, which is in agreement with previous reported results[10]. Though SEI film resistance and bulk resistance increased at low temperatures, the increase was insignificant as compared to charge transfer. Hence, it can be concluded that the low capacities of these two anodes at -30°C as compared to 25°C, is mainly due to the increased charge transfer resistance. This confirms the influence of ceramic on improving the electrochemical kinetics at low temperatures. Higher Li ion conductivity and higher specific capacity of this anode at low temperatures makes it suitable for solid polymer electrolyte cells.
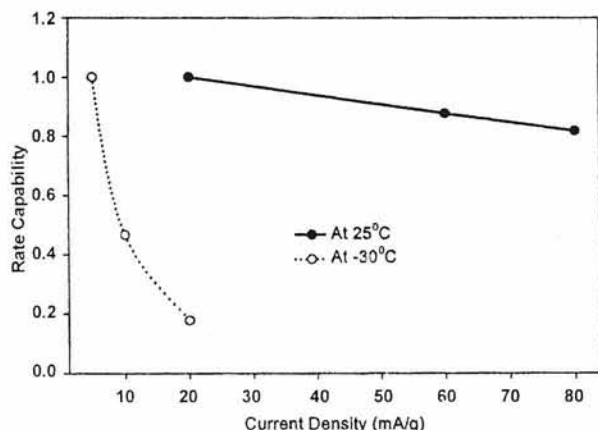
Fig. 8 – Rate capability of Graphite ks-4 (50%) - nano Si (10%) – ceramic (20%) – PEO-LiClO$_4$ (20%) anode at 25°C and -30°C as a function of current density.

Rate capabilities of graphite ks-4 (50%) nano Si (10%) – ceramic (20%) – PEO-LiClO$_4$ (20%) anode at 25°C and -30°C

Electrochemical impedance studies show that the addition of high Li-ion conducting ceramic into graphite-nano silicon anodes can largely improve the reaction kinetics of the electrodes, which may result in a high rate capability. The rate capability of electrodes at room temperature is defined as the ratio of charge capacity at a specific current density to the charge capacity obtained at 20 mA/g. Similarly, for -30°C, ratio of charge capacity at a specific current density to the charge capacity obtained at 5 mA/g was defined as rate capability. At 25°C and at -30°C, graphite ks-4 (50%) nano Si (10%) – ceramic (20%) – PEO-LiClO$_4$ (20%) anode was discharged-charged at different current densities. These relative charge capacities are plotted as a function of current density in Fig. 8. At 25°C and at 20 mA/g current density, nano Si 10% anode with the above composition showed a charge capacity of 300 mAh/g. At 60 mA/g current density, it showed a capacity of 263 mAh/g, and a relative capacity of 0.87. At 80 mA/g current density, it showed a capacity of 245 mAh/g and a relative capacity of 0.81. These high relative capacities of nano Si 10% anode showed a high rate capability at room temperature. This is attributed to the fast reaction kinetics. At -30°C, when charged – discharged at 5 mA/g current density, nano Si 10% anode exhibited a charge capacity of 161 mAh/g. At 10 mA/g current density, it showed a charge capacity of 75.12 mAh/g, resulting in a relative capacity of 0.46. At 20 mA/g current density, it showed a charge capacity of 48 mAh/g, which is equivalent to a relative capacity of 0.17. Usually, graphite anodes

cannot be discharged and charged at -30°C using current densities more than 5 mA/g (ref. 8). High charge capacity (161 mAh/g) and better rate capability of nano Si 10% anode at -30°C can be attributed to the improved electrochemical kinetics resulting from the addition of ceramic powder. Ceramic powder has a lower activation energy (<0.3eV) which makes it highly Li ion conductive even at a temperature of -30°C. As mentioned above, at low temperatures, in high density thin films, Li ion transfer through liquid electrolyte is limited. The only way for Li transportation from liquid electrolyte to surface of the active particles is through an ionic conducting carrier. Here, the ceramic works as a carrier because of its high Li ion conductivity at low temperature. Due to improved Li ionic transport, the kinetics of the electrochemical reactions is also improved.

Conclusions

A new Si/G composite anode has been prepared and its electrochemical performance tested in the temperature range -40°C to 45°C. At room temperature, anode with a composition of graphite ks-4 (50%) – nano Si (10%) – ceramic (20%) – PEO-LiClO$_4$ (20%) shows an initial charge capacity of 560 mAh/g and a stable reversible capacity of 302 mAh/g after 50 cycles. However, it shows a severe capacity fade during the initial 5 cycles. This may be attributed to poor mechanical strength of polymer binder. Regardless of the low capacity of the anode at 25°C, when discharged – charged at 5 mA/g current density at -30°C, this anode exhibits a charge capacity of 160 mAh/g. The anode also shows high rate capability at 25°C and -30°C. The high rate capability and excellent low temperature performance of the anode may be attributed to improved charge transfer kinetics resulting from high Li ion conductivity of the ceramic powder. High rate capability and excellent low temperature performance of this anode makes it suitable for NASA aerospace applications.

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