Composite anode material with mixed conductivity for solid state lithium ion battery

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Abstract

A composite silicon-carbon (SCM) anode material with high ionic and electronic conductivity for solid polymer Li-ion batteries has been investigated, and its performance at different temperatures (-30^{0}C & 25^{0}C) and different current densities was analyzed using various electrochemical methods. A high density thin film with a composition of graphite-nano-silicon-ceramic-PEO+$LiClO_4$ was used as anode. Electrochemical behavior of composite anodes with different Si compositions and different ceramic compositions was studied. Composite anode with a composition of Graphite (50%)-Si (10%)-Ceramic (20%)-PEO+$LiClO_4$ (20%) showed a stable reversible capacity of 300 mAh/g over 60 cycles at room temperature and a reversible capacity of 172 mAh/g at -30^{0}C.

1. Introduction

Si/C composite anode materials have received increasing attention as alternatives to carbon/graphite for Li-ion rechargeable batteries due to their high specific energies and energy densities. There is considerable research being conducted to increase the specific capacity and improve the cycling performance of these anodes. Various groups like Yang et al, Kim et al, Liu et al, Wang et al and Dimov et al have prepared SCM anodes by various methods which showed a stable reversible capacity of 700 mAh/g over 30 cycles. As of now these anodes can be used only in liquid electrolyte cells. In case of solid state batteries, solid electrolyte has low Li ion conductivity which results in low specific capacities. To improve the performance, anode should have high Li ion conductivity, high electronic conductivity and high reversible capacity. The objective of this work is to meet the NASA requirements for anode in solid state Li ion battery with excellent low temperature performance. In this study we prepared a new SCM anode by using a ceramic powder and a Li-ion conductive polymer as a binder. The electrochemical performance of these anodes at room temperature and low temperature are presented here.

2. Experimental

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) & Phosphorous pentasulfide (Aldrich) powders in 8:2 molar ratios were ball milled for 12h and then heat treated at 300^{0}C for 2h to form a high Li-ion conductive ceramic powder. KS4 Graphite (TIMCAL GROUP, Switzerland), nano Si (30-70nm, Nanostrucutred & Amorphous Materials Inc), $80Li_2S{\cdot}20P_2S_5$ 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. The composite was then mechanical milled for 5 min outside of glove box to obtain homogeneous composite slurry. Then the slurry was rolled 4-5 times to form a composite anode (50um). To remove the excess AcetoNitrile solvent, anodes were dried in a vacuum oven at 80^{0}C. Then these dry anodes were pressed to enhance the contact between the active materials and the conductive graphite. Mixing of $80Li_2S{\cdot}20P_2S_5$ with G-Si-PEO composite anodes was done to increase the ionic conductivity of the anode and improve the low-temperature performance of anodes. Li ion conductive $LiClO_4$-PEO polymer is used as a binder to further improve the ionic conductivity of composite anode. The CR2032 coin cells

were assembled inside the Glove box using Li metal as counter electrode and 1M $LiPF_6$/EC/DEC/DMC/EMC (1:1:1:3 by volume) (Ferro Corporation) as electrolyte. $LiPF_6$/EC/DEC/DMC/EMC can be used as electrolyte even at the temperature below -30°C because of the existence of liquid phase even at a low temperature of -40°C. The cells were galvanostatically charged and discharged in the range of 0-1.5V at a current density of 20 mAh/g.

2. Results and Discussion

Influence of Ceramic on reversible capacity

Fig. 1 shows the influence of ceramic on reversible capacity of KS4 graphite and SCM anodes. Four cells were prepared by using KS4 graphite and Si/KS4 graphite with and with out ceramic addition. KS4 graphite (70%), PEO+$LiClO_4$ (30%) anode exhibited a Li-insertion (discharge) capacity of 517 mAh/g and a Li-extraction (charge) capacity of 230 mAh/g, resulting in an irreversible capacity loss of 55.4%. Addition of ceramic (20%) to KS4 graphite resulted in a Li-insertion capacity of 635 mAh/g and a Li-extraction capacity of 360 mAh/g. The addition of ceramic (20%) to KS4 graphite decreased the irreversible capacity of anode from 55.4% to 43.2%. Moreover, addition of 20 wt% nano-Si into KS4 graphite (70%)-(PEO+$LiClO_4$) (30%) showed a discharge capacity of 1058 mAh/g and a charge capacity of 470 mAh/g resulting in an irreversible capacity loss of 55.52%. Similarly, addition of 20 wt% nano-Si to KS4 graphite (40%), Si (20%), Ceramic (20%) & PEO+LiClO4 (20%) anode exhibited a discharge capacity of 1132 mAh/g and a charge capacity of 707 mAh/g resulting in irreversible capacity loss of 37.54%. These results show that addition of ceramic resulted in increase of discharge capacity, and reduction of irreversible capacity. This is because of the high Li-ion conductivity of $80Li_2S{\cdot}20P_2S_5$ which enhanced the Li insertion/extraction kinetics of composite anodes.

Electrochemical performance of SCM anodes with different Si content:

To determine the effect of Si content on cycling performance, electrodes with different Si composition (10%, 15%, 20% & 25%) were tested as shown in Fig 2. Among all the electrodes, Si 20% electrode showed highest initial charge capacity of 1608 mAh/g. As the Si content in the anode increased, initial irreversible capacity also increased. Anode with Si 25% showed the highest irreversible capacity of 926 mAh/g and Si 10% showed lowest irreversible capacity of 267 mAh/g. Even though higher capacity is obtained with higher Si content, it also resulted in degradation of cycling performance. Anode with Si 10% showed a stable reversible capacity of 300 mAh/g for 61 cycles. Anode with Si 15% showed a stable reversible capacity of 260 mAh/g for 22 cycles. Anodes with Si 20% & 25% exhibited a poor cycle life of 7 cycles. This may be due to the spallation of Si particles from the thin film caused by large volume expansion. From the above results, it is evident that Graphite ks-4 graphite (50%), Si (10%), Ceramic (20%), PEO+LiClO4 (20%) anode showed the best capacity retention and cycling performance.

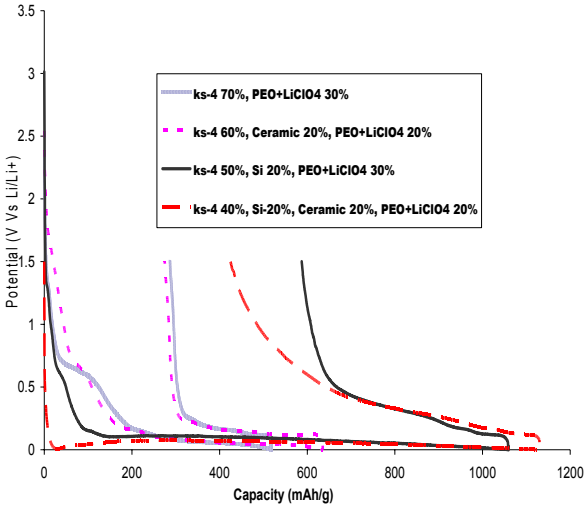

Fig 1: Charge-discharge curves for anodes With and with out Ceramic content

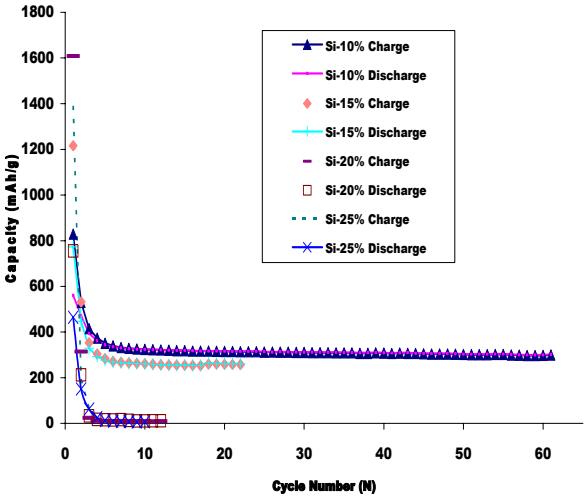

Fig 2: Cycling performance of anodes with different Si Composition

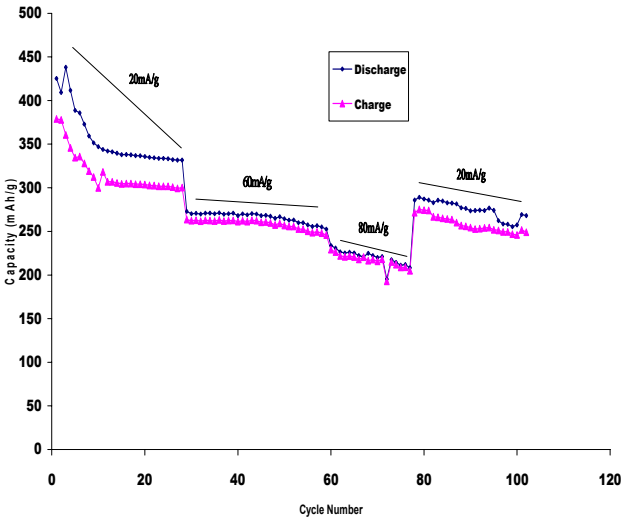

Fig 3: Cycling performance of Si-10% anode at different current densities

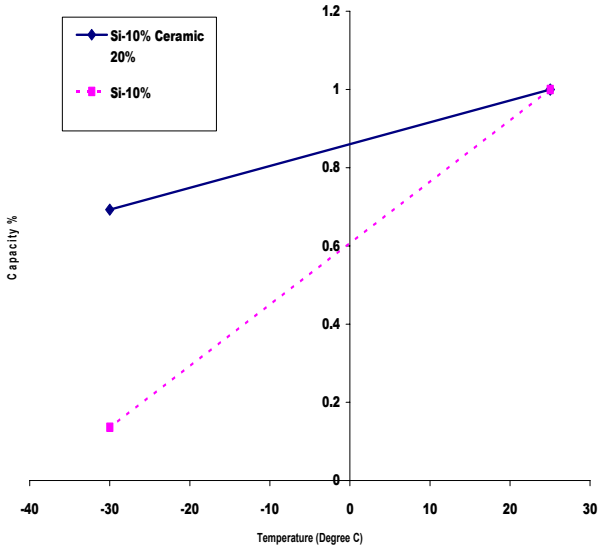

Fig 4: Capacity % Vs Temperature Si-10% anodes with & with out ceramic

Performance of Si 10% anode at different current densities:

Fig 3 shows the charge-discharge capacities of Si 10% anode at various current densities as a function of cycle number. The anode showed a discharge capacity of 300 mAh/g at a current density of 20 mAh/g, 263 mAh/g at a current density of 60 mAh/g and 233 mAh/g at a current density of 80 mAh/g. The high rate capability of composite anode is attributed to the fast reaction kinetics of anodes.

Low temperature performance of Si 10% anode:

Fig 4 shows the ratios of capacity at different temperatures to capacity at room temperature for anodes with different ceramic composition. KS4 graphite (60%), Si (10%), PEO-$LiClO_4$ (30%) anode exhibited a reversible capacity of 20 mAh/g at -30^{0}C which is 12.3% of the capacity at 25^{0}C. By the addition of ceramic, reversible capacity at -30^{0}C has increased to 172 mAh/g, which is 69% of the capacity of the anode at 25^{0}C. It shows the influence of ceramic on low temperature performance improvement which is due to the low activation energy of ceramic powder at low temperatures resulting in high Li ion conductivity.

Conclusions

A new type of Si/C composite anode was prepared by using graphite, nano Si, ceramic powder, PEO and $LiClO_4$. Anodes with different Si content were prepared and anode with Si 10% composition showed better capacity retention and cycling performance. Addition of the ceramic powder has improved the reversible capacity and low-temperature performance. It showed a reversible capacity of 172 mAh/g at -30^{o}C which is 69% of capacity of the anode at room temperature. This is attributed to high ionic conductivity of ceramic powder which in turn increased the lithium insertion rate. The excellent low temperature performance and cycling performance makes this composite anode suitable for NASA applications.

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