

Synthesis and electrochemical characterization of novel high capacity $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode for rechargeable lithium batteries

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Abstract

An innovative $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound has been identified as possible anode for rechargeable lithium batteries. The compound was synthesized (ceramic method), characterized (PXRD, SEM), and evaluated for electrochemical performance behavior (charge–discharge). The $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode exhibited higher specific capacity (470 mAh/g) and an acceptable capacity fade (<20%) upon extended cycling. The coulombic efficiency of the compound was found to be 99% even after 50 cycles. The lower average oxidation number and the higher ionic radius of Fe dopant were believed to restrict the formation of passivating surface film and reduced the capacity fade of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode upon cycling.

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1. Introduction

With a view to combat the low energy density problems of carbonaceous anodes in lithium-ion batteries, a variety of metal oxides [1,2], ternary metal vanadates [3,4] and lithiated metal nitrides [5,6] are being examined for possible electrochemical and better anode performance characteristics. Among these candidates, hexagonal Li_3N anodes have gained paramount importance in the recent years, due to their high capacity capabilities [7,8]. However, requirement of stringent synthesis conditions and the uncontrollable capacity degradation problems [9] of $\text{Li}_{3-x}\text{M}_x\text{N}_4$ are the hampering issues against the wider acceptance of such an-

odes for practical applications. Therefore the present study was aimed at the identification of novel and a suitable $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode for lithium-ion batteries, which may be synthesized by an easy-to-adopt ceramic method, wherein the moisture sensitivity problems related to Li_3N anodes are surpassed eventually. That is with a deep concern to decrease the Li–N interaction, the study explores the possible formation of silicon defective electrode material through the synthesis of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$, wherein the dopant metal Fe partially replaces the silicon present in the trigonal Si_3N_4 matrix, thereby alleviating the moisture sensitivity problems of $\text{Li}_{3-x}\text{M}_x\text{N}_4$ type anodes. The effect of Fe dopant in improving the electrochemical characteristics of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode has been understood through systematic physical as well as electrochemical characterization and a comparison of electrochemical performance of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode with that of the parent Si_3N_4 compound.

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2. Experimental

2.1. Synthesis procedure

A mixture of Si_3N_4 and iron powder ($x = 0.04$) was ground well using an agate mortar (30 min) and pelletised by applying a pressure of 25 MPa in a hydraulic press. The pellet was heat treated initially to 300 °C (24 h) and further to 800 °C (3 h) in the nitrogen atmosphere with frequent intermittent grinding for every 8 h calcination time. The ultra fine powders collected from furnace were ground and subjected to characterization studies.

2.2. Structural and morphological characterization

Phase characterization was done by powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 10–110° at a scan rate of 0.1°s^{-1} . Surface morphology of the particles was examined through SEM images obtained from Jeol S-3000 H Scanning Electron microscope and the charge–discharge studies were carried out using MACCOR charge–discharge cycle life tester.

3. Electrochemical characterization

The anode electrode was prepared and used as described elsewhere [10].

4. Results and discussion

4.1. Structural results – PXRD studies

The PXRD pattern recorded for Si_3N_4 , Fe and $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ are depicted in Figs. 1(a)–(c). Generally, the effect of Fe dopant is expected to change or enhance the intensity of the basic peaks observed for Si_3N_4 compound (Fig. 1(a)) along with the appearance of characteristic peaks of Fe (Fig. 1(b)). Interestingly, the same has been observed with the XRD pattern of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound (Fig. 1(c)), thus substantiating the fact that Si_3N_4 with a trigonal structure (*space group: $p\bar{3}1c$*) has formed a solid solution with iron, without changing the basic peak pattern of the same. The perfect matching of observed Bragg peaks, absence of additional peaks due to undesirable impurities are in favor of single phase formation of pure $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound. Further, the presence of sharp and intense nature of XRD peaks (Fig. 1(c)) confirmed the better crystallinity of synthesized $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ powders.

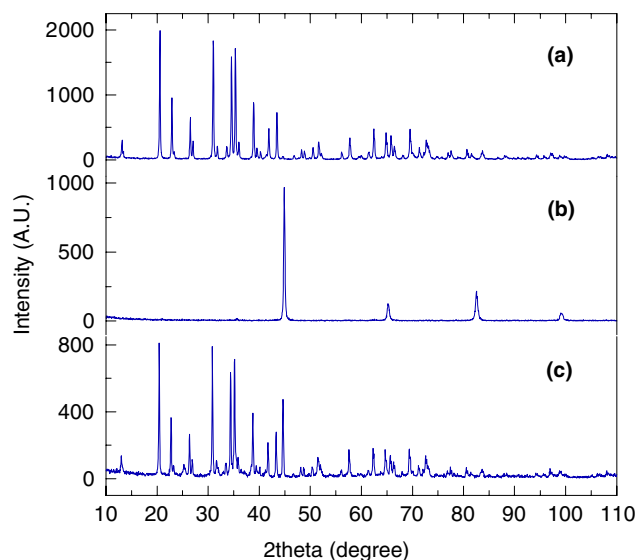


Fig. 1. XRD pattern exhibited by (a) Si_3N_4 , (b) Fe powder, and (c) $\text{Si}_{3-x}\text{M}_x\text{N}_4$.

4.2. Morphological results – SEM analysis

SEM image of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ contains (Fig. 2) uniformly distributed un agglomerated independent grains of clearly seen crystal facets. The absence of agglomeration (made possible even at 800 °C calcination) and the presence of grain growth controlled particles of sub-micron size are in favor of structurally and electrochemically favored morphology feature for the better anode performance characteristics of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound.

4.3. Electrochemical characterisation results

When the stable existence of Fe in the ionic crystal is concerned, $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compound seems to have some sort of Si defect or distribution, which may not be ignored. However, such a behavior of Si is expected to

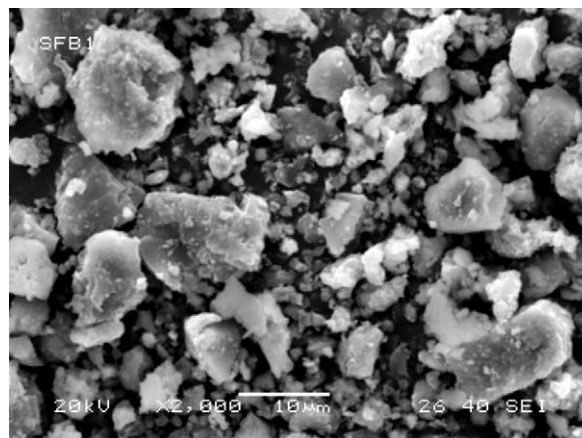


Fig. 2. SEM photograph of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound.

result in the formation of additional vacant sites in the basic matrix of the Si_3N_4 compound, which in turn may act presumably as lithium intercalation/red-ox centers. Based on these grounds, the synthesized $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound is expected to exhibit possible electrochemical performance characteristics against lithium metal.

4.3.1. Charge–discharge studies

To understand the effect of Fe dopant in improving the electrochemical properties of Si_3N_4 anode, two types of cells, viz., $\text{Li}|\text{Si}_3\text{N}_4$ and $\text{Li}|\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ half-cells were fabricated and subjected to charge–discharge studies at a constant ($C/10$) current rate. The charge–discharge curves obtained for Si_3N_4 and $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compounds cycled between 0 and 3.3 V are furnished in Figs. 3(a) and (b). Basically, the potential profile of Si_3N_4 and $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anodes exhibited plateau around 0.7 and 0.9 V respectively, which is much lower than the $\text{Li}_3\text{N}/\text{Li}_{3-x}\text{M}_x\text{N}$ type of anodes [1,3], thus qualifying themselves as better anodes. Also, the appearance of potential plateau and the discharge pattern exhibited by Si_3N_4 and $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anodes (Figs. 3(a) and (b)) may be attributed to the change of structure from crystalline

to amorphous phase, which is believed to be maintained upon further cycling, as evidenced by the subsequently reduced capacity fade values observed from second cycle onwards. Interestingly, the initial capacity of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound was found to be 470 mAh/g (Fig. 3(b)) which is about 4.7 times higher than the initial capacity (100 mAh/g) of the undoped Si_3N_4 compound (Fig. 3(a)). The lower average oxidation number and the higher ionic radius of Fe compared to Co and Ni metals are believed to be responsible for the considerably improved specific capacity values of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode. Despite the larger initial irreversible capacity loss behavior of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode, the possible formation of surface film is believed to be restricted due to the presence of Fe dopant, thus corresponds to the reduced capacity fade upon extended cycling. Similarly, the short-range ordering with respect to the amorphous nature of the $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound after lithium interaction is also expected to follow a favorable rearrangement of elements so as to reduce the capacity fade upon cycling. As a result, the capacity of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode after 50 cycles was found to be 210 mAh/g, which is about 2.5 times higher than the parent Si_3N_4 compound and the coulombic efficiency was found to be 99% (Fig. 4). Further, the potential plateau observed at 0.9V region is very much lower than the ever reported $\text{Li}_3\text{N}/\text{Li}_{3-x}\text{M}_x\text{N}$ type of anodes [11], thus qualifying the explored $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode as a better candidate for exploitation towards practical lithium-ion battery applications. Thus the anode performance behavior of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound is understood as a function of inherent nature of the iron dopant and the preferred surface morphology produced via systematically adopted synthesis methodology with the deployment of intermittent grinding of reactant particles. On the other hand, no improvement in the initial irreversible capacity loss value has been observed, thus triggers the need for further detailed work on this compound, which is in progress.

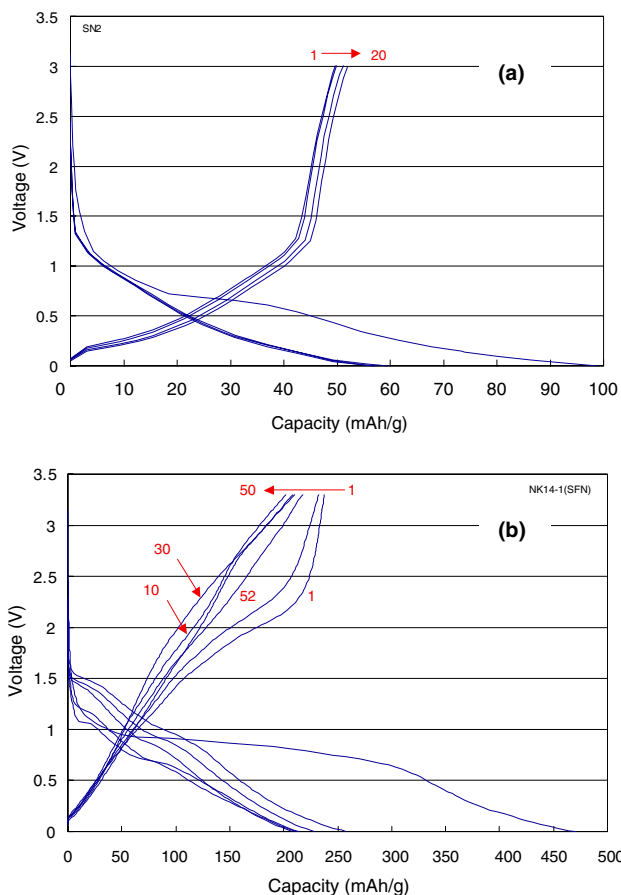


Fig. 3. Charge–discharge behavior of $\text{Li}|\text{Si}_3\text{N}_4$ and $\text{Li}|\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ cells.

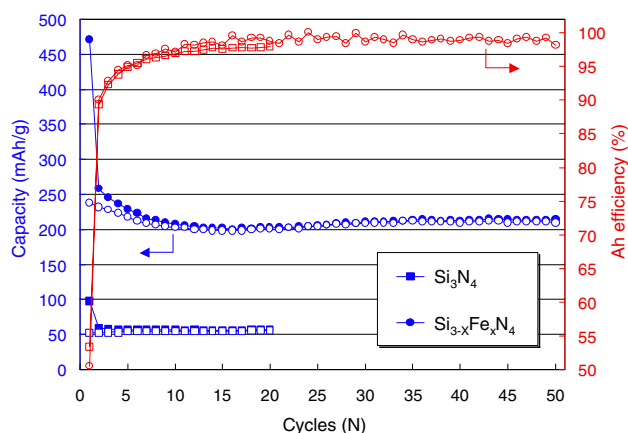


Fig. 4. Capacity comparison of $\text{Li}|\text{Si}_3\text{N}_4$ and $\text{Li}|\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ cells.

5. Conclusion

A novel category $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound has been explored as an alternative lithium battery anode, via. synthesis, characterization and electrochemical evaluation of the same against lithium metal. The identified $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode exhibited a specific capacity of 470 mAh/g and a reduced capacity fade upon subsequent cycles ($\leq 20\%$) with 99% coulombic efficiency. The high capacity values and the reduced capacity fade characteristics of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode may be exploited for rechargeable lithium battery applications.

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