

Short Communication

Synthesis and Characterization of Newly Identified $\text{Si}_{3-x}\text{M}_x\text{N}_4$ (M= Co, Fe) Anodes for Lithium Batteries

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Abstract: A novel category Si_3N_4 anode and a series of doped derivatives of silicon nitride with a general formula $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [M= Co and Fe] were identified as possible anode materials for rechargeable lithium batteries through the present study. The compounds were synthesized via solid-state fusion method and characterized for phase purity and surface morphology through XRD and SEM respectively, prior to electrochemical performance analysis. The compound Si_3N_4 exhibited inferior capacity (~100mAh/g) whereas the metal doped nitrides, viz., $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [M= Co and Fe] exhibited improved specific capacity values in the range of 130-470 mAh/g, with lesser capacity fade (<20%) after 50 cycles. More specifically, the $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode with a specific capacity of ~ 470mAh/g may be exploited for practical applications. The effects of individual dopants in enhancing the electrochemical behavior of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ anodes are discussed.

Keywords: semiconductors, chemical synthesis, scanning electron microscopy, specific capacity

1. INTRODUCTION

Lithium-ion batteries, which are based on the intercalation process of lithium into carbonaceous anodes perform well in terms of cycleability along with an unavoidable low energy density problem. Recently, ternary lithium metal nitrides of both antifluorite [$\text{Li}_{2-n}\text{MN}_n$ type] and hexagonal structure [Li_3N type] were found to exhibit good electrochemical cycling behavior [1-4]. Among the two types of compounds, the hexagonal Li_3N category, which is composed of $\text{Li}_2^+\text{N}^{3-}$ layers [5] were found to exhibit higher capacity [6]. However, requirement of stringent synthesis conditions that are required to prepare $\text{Li}_{3-x}\text{M}_x\text{N}$ anodes and the comparatively poor cycle life performance of such anodes have triggered the need to examine and explore the possibility of employing some novel category anodes. Hence a study on the synthesis and characterization of series of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [M= Co, Ni, Fe] compounds as possible lithium battery anodes is sought in the present investigation. Taking into consideration the fact that enhanced lithium-ion migration and creation of lithium defects which are possible in lithium-ion systems due to the decreasing Li-N interaction [7,8], the present study aims at the exploitation of Si_3N_4 and $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [M=

Co, Ni, Fe] anodes, instead of Li_3N related anodes. The current work is undertaken primarily with a view to reduce the Li-N interaction, via formation of silicon defective electrode matrix and to circumvent the moisture sensitivity problems related to the synthesis of lithium nitride anodes possibly. In particular, the study deals with the synthesis, characterization and electrochemical evaluation of Si_3N_4 and $\text{Si}_{3-x}\text{M}_x\text{N}_4$ category anodes individually in order to understand the effect of individual dopants in modifying the electrochemical characteristics.

2. EXPERIMENTAL

2.1. Synthesis procedure

A mixture of Si_3N_4 and respective metal powders, viz., cobalt, nickel or iron ($x = 0.4$) was ground in an agate mortar for about 30 minutes, pelletized by applying a pressure of 25 MPa in a hydraulic press and the pellets were heat treated initially to 300°C for 24h, with nitrogen gas atmosphere. The heat treated powders were ground again to re assure intimate and homogenous mixing of the precursors during and/or after the process of furnace heating at low temperature(300°C). Subsequently, the powders were subjected to intermittent grinding after every 8h interval and were subjected further to high temperature calcination at 800°C for 3h in

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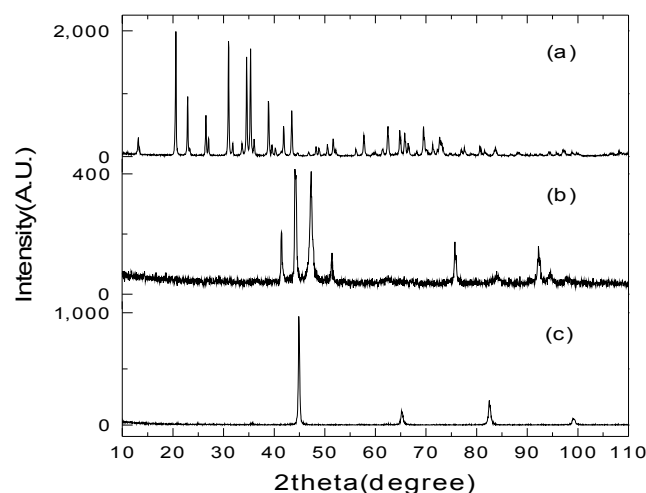


Figure 1. XRD patterns of raw materials; (a) Si_3N_4 , (b) Co, (c) Ni, (d) Fe powder

nitrogen gas atmosphere. The final products recovered from the furnace were ground and subjected to various 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 Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of $10\text{--}120^\circ$ at a scan rate of $0.1^\circ/\text{sec}$. Surface morphology of the particles was examined using SEM images obtained from Jeol S-3000 H Scanning Electron microscope. Charge-discharge studies were carried out using MACCOR charge-discharge cycle life tester and the CV studies were performed with IM-6 Electrochemical Impedance Spectrometer.

2.3. Electrochemical characterization

The anode electrode was prepared by the method described elsewhere [9]. The moisture controlled electrodes were used against a lithium foil of thickness $120 \mu\text{m}$, an electrolyte of 1:1 v/v EC:DEC dissolved in 1M LiPF_6 and a polypropylene separator (Asahi) of $20 \mu\text{m}$ thickness with 40% porosity. The fabricated pouch cells were kept in the dry room for one day (aging process) before subjected to charge-discharge analysis.

3. RESULTS AND DISCUSSION

3.1. Structural results - PXRD studies

The PXRD pattern recorded for the parent compound Si_3N_4 and the dopant metals selected for the present study, namely Co and Fe are depicted in Figs.1a-c respectively. When the observed bragg peaks of Si_3N_4 (Fig.1a) were indexed for a trigonal structure of JCPDS pattern, a perfect match in the peak pattern was observed with the standard one. Therefore, it is understood that Si_3N_4 compound has a trigonal structure (space group: $p31c$) [10], wherein possibilities to partially accommodate the mentioned dopants for Si appears to be appreciable[1]. Eventually, the effect of incorporated dopant(s) are expected to change or enhance the

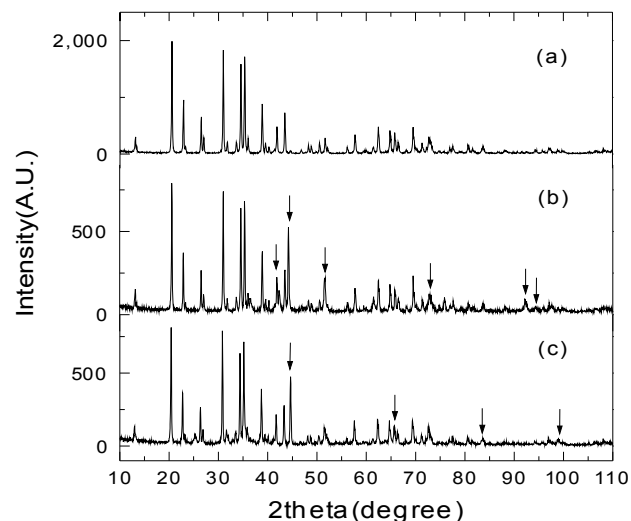


Figure 2. XRD patterns of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds; (a) Si_3N_4 , (b) $\text{M}=\text{Co}$, (c) $\text{M}=\text{Fe}$

intensity of the basic peaks observed for Si_3N_4 compound, along with the appearance of newer and characteristic peaks of dopant metal(s) at appropriate positions in the final products. Interestingly, the same has been observed with the present set of newly identified $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds (Figs.2b&c), without changing the basic Bragg pattern of the parent Si_3N_4 compound. Thus it is implied that the dopants (Co or Fe) have successfully been incorporated into the trigonal matrix of Si_3N_4 compound. Also, it is understood that the system Si_3N_4 forms a solid solution wherein the presence of Si in the Si_3N_4 structure may partially be substituted by Co or Fe. It is noteworthy that the upper solubility limit of the system is yet to be identified and the present study is restricted, especially with the preliminary understanding of possible existence of solid solutions of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds, with respect to the mentioned limit of dopant concentration. Interestingly, no extra peaks were identified in the PXRD pattern recorded for the entire set of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds (Figs.2b&c), which is an indication of phase purity of the final products. Also, the Bragg peaks exhibited by Si_3N_4 and the solid solutions of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [$\text{M} = \text{Co, Fe}$] type were found to be sharp and intense in nature, thus accounting for the better crystallinity of the synthesized products.

3.2. Morphological results - SEM analysis

SEM images of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [$\text{M} = \text{Co, Fe}$] compounds are appended in Figs. 3a&b. The metal doped silicon nitrides are found to contain uniformly distributed spherical grains of clearly seen crystal boundaries, as evident from Fig.3. However, a slight difference in the size of the individual grains ($5\text{--}10 \mu\text{m}$) is observed with the SEM images of $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ and $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compounds [Figs. 3a&b]. Therefore, it is understood that despite the deployment of similar calcination conditions towards the synthesis of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds [$\text{M} = \text{Co, Fe}$], the surface morphology of the final products vary as a function of inherent nature of the individual dopants. However, absence of obviously agglomerated particles and the appearance of growth controlled particles with

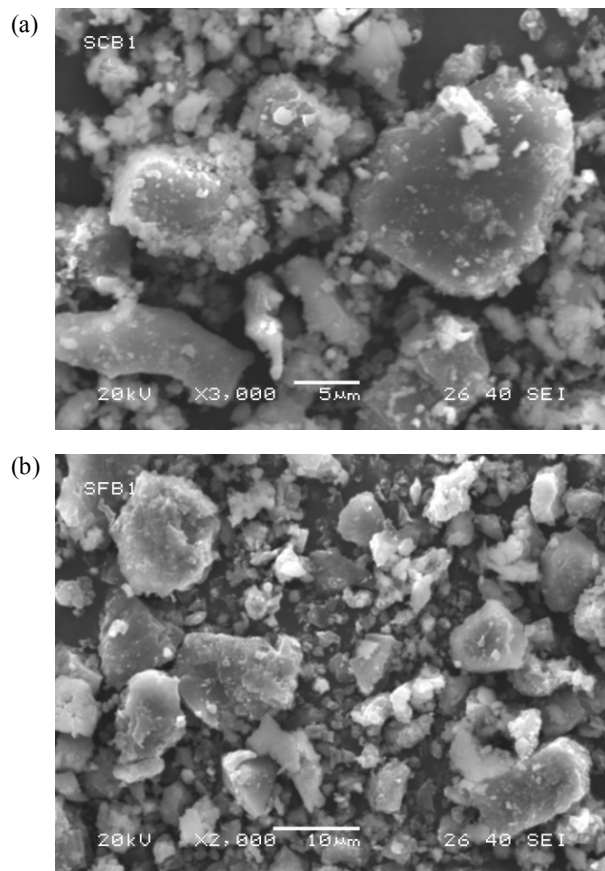


Figure 3. SEM photographs of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds; (a) $M=\text{Co}$, (b) $M=\text{Fe}$

confined crystal facets (Figs.3a&b) are in support of both structurally and electrochemically favored surface morphology features of the $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [$M = \text{Co}, \text{Fe}$] compounds.

3.3. Electrochemical characterisation results

While considering the stable existence of M ions in the ionic crystal, $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds may have some sort of Si defect or distribution, which cannot be ignored. Consequently, such a behavior of Si is expected to 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 $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [$M=\text{Co}, \text{Fe}$] compounds are expected to exhibit possible anode performance characteristics against lithium metal.

3.3.1. Charge-discharge studies

To understand the effect of individual dopants in improving the electrochemical behavior of Si_3N_4 anodes, a series of $\text{Li}/\text{Si}_3\text{N}_4$, $\text{Li}/\text{Si}_{3-x}\text{Co}_x\text{N}_4$ and $\text{Li}/\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ 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 compounds cycled between 0-3.3V are furnished in Figs.4a-c. Initially, the voltage of Si_3N_4 drops suddenly (up to 1.2V), followed by a small plateau

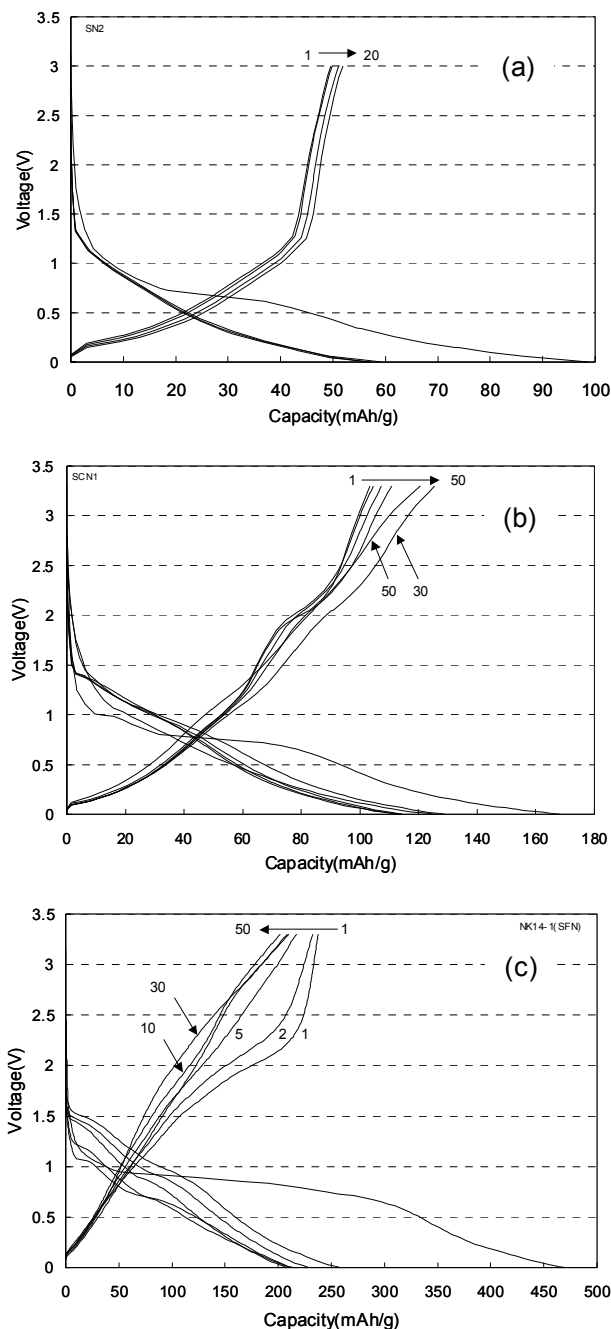


Figure 4. Voltage profiles of $\text{Li} | \text{Si}_{3-x}\text{M}_x\text{N}_4$ cells; (a) Si_3N_4 , (b) $M=\text{Co}$, (c) $M=\text{Fe}$

(0.7V), and finally the cell voltage decreases gradually (Fig.4a). Such type of discharge behavior of Si_3N_4 anode may be attributed to the combined effect of change of structure from crystalline to amorphous state, and to a possible change of surface morphology [11], presumably due to the formation of protective surface film over the anode electrode. Despite the lower initial capacity (~100mAh/g) of Si_3N_4 anode, an increase in capacity has been observed upon progressive cycling, which may be attributed to the

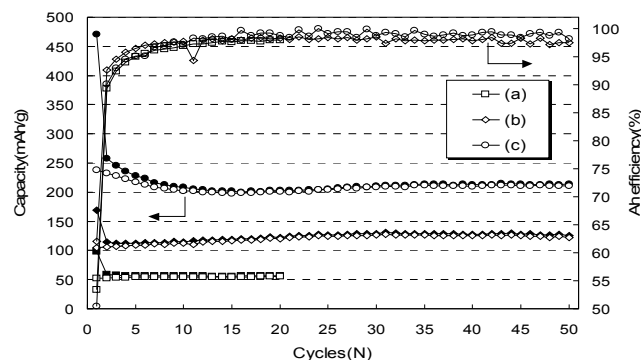


Figure 5. Capacity comparison of $\text{Li} | \text{Si}_{3-x}\text{M}_x\text{N}_4$ cells; (a) Si_3N_4 , (b) $\text{M}=\text{Co}$, (c) $\text{M}=\text{Fe}$

electrochemically driven size confinement of the particles, otherwise known as the electrochemical grinding of electrode material to form nano particles [12]. As a result, the capacity loss was found to get reduced to the extent of 15% (from 55%) after 10 cycles, thus showed marked improvement in the coulombic efficiency upon cycling.

Figs.4b&c represent the charge-discharge behavior of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds with $\text{M} = \text{Co}, \text{Fe}$ respectively. It is evident from the figure that the small plateau region of the charge-discharge curves exhibited by $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [$\text{M} = \text{Co}, \text{Fe}$] compounds substantiates the involvement of two phase [11] reaction during the intercalation/de-intercalation process. i.e., the structure of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ [$\text{M} = \text{Co}, \text{Fe}$] compounds changes from crystalline to amorphous phase in the first cycle and the amorphous state is expected to be maintained upon extended cycling. Also, the potential plateau of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds (Figs.4b&c) as observed below 1V (0.7 ~ 0.9V), 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.

More interestingly, the initial capacity of $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ compound was found to be 170mAh/g, which is about 1.7 times higher than the initial capacity of Si_3N_4 anode. Also, a gradually increasing capacity behavior was observed from second cycle onwards and the capacity of $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ anode (Fig.4b) after 50 cycles (123mAh/g) was found to be higher than the initial charging capacity (~100mAh/g) of Si_3N_4 anode. Hence, it is understood that the cobalt dopant has modified the magnitude of realizable capacity to a considerable extent along with a reduced fade in capacity (< 15%) upon cycling (Fig.5). Incidentally, a possible and a fundamental rearrangement of elements that is concerned with the short-range ordering of amorphous state of silicon metal nitride derivatives is expected to occur [13], which is responsible for the increase in capacity of $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ anode upon cycling. Further, the maintenance of amorphous phase upon extended cycling may be attributed to the reduced capacity fade observed with $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ compound.

Interestingly, $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ compound exhibited the highest initial discharge capacity of ~ 470mAh/g, which is about 4.5 times higher than the parent Si_3N_4 anode. Further, capacity fade upon cycling was found to get minimized (15% after 50 cycles), similar to that of $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ anode (Fig.5), albeit the smaller decrease in the specific capacity values observed on extended cycles. i.e., the capacity

after 50 cycles was found to be 210 mAh/g, which is considerable higher than the parent Si_3N_4 and the $\text{Si}_{3-x}\text{Co}_x\text{N}_4$ anodes. The lower average oxidation number and the higher ionic radius of Fe compared to Co metal are believed to be responsible for the improved specific capacity values and the reduced capacity fade behavior of $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anodes, via. restricted formation of passivating surface film. Thus, the difference in the electrochemical behavior of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds with $\text{M} = \text{Co}, \text{Fe}$ (Fig.5) may very well be understood as a function of observed differences in the surface morphology patterns and the inherent nature of the individual metal dopants.

4. CONCLUSION

A series of novel category Si_3N_4 and $\text{Si}_{3-x}\text{M}_x\text{N}_4$ anodes containing $\text{M} = \text{Co}, \text{Fe}$ has been synthesized and evaluated for electrochemical performance characteristics. All the compounds exhibited reversible electrochemical (intercalation/de-intercalation) behavior and the $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anode showed the highest specific capacity, even after the expense of 50 cycles. Both dopants, namely Co and Fe were found to be effective in improving the specific capacity values of $\text{Si}_{3-x}\text{M}_x\text{N}_4$ derivatives along with a lesser capacity fade upon extended cycling compared to the parent Si_3N_4 compound. Hence the present study recommends the series of Si_3N_4 and $\text{Si}_{3-x}\text{M}_x\text{N}_4$ compounds with $\text{M} = \text{Co}, \text{Fe}$ as possible alternative anodes and more specifically, the $\text{Si}_{3-x}\text{Fe}_x\text{N}_4$ anodes for their high capacity capabilities to be exploited possibly in rechargeable lithium batteries.

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