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Theoretical Analysis of Stresses in a-Si Electrodes of Sodium-ion Batteries During Charging and Discharging

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Abstract:- Advanced electrochemical energy storage technology is used extensively to overcome the concerns related to depletion of fossil fuels and increasing environmental pollution. Among these Li-ion batteries are one of the promising batteries currently used. However the limited and expensive lithium resources have led to a need of looking beyond the Li-ion batteries. In this view, sodium ion battery technology is emerging as promising alternative in the current EES technology. For developing such batteries, the main issue that is faced is the larger 'ionic radius' of Na + in contrast with 'ionic radius' of Li + . Due to this generally used graphite as anode material for Li-ion battery is not acceptable for Na-ion battery. Thus, research activity to find an appropriate anode material for Na-ion battery is extensively done. From the few alloying reaction based anode materials, amorphous silicon is used in this paper. Use of a-Si for Na-ion batteries causes capacity fade during sodiation/desodiation cycles. The important cause for this is volumetric changes during the Na-insertion and removal which can lead to stress developments, capacity fade and fracture of electrode. This issue for Na-ion batteries can be fairly said is yet unexplored. The present study predicts the theoretical stresses during elastic and plastic deformation induced in a-Si films during sodiation/desodiation cycles. This study addresses one of the bottlenecks towards successful design and development of the stable anode material for relatively more sustainable Na-ion batteries.

***Keywords**:- Sodium ion battery, Amorphous Silicon, Stress in Na 0.76 Si, State of Charge.*

I. INTRODUCTION

The Lithium resources on the Earth are shrinking along the years at a very massive pace. Thus, looking beyond the Li-ion batteries has become a major need. In view of this,Sodium ion battery technology is emerging as promising alternative in the current EES technology For developing Na-ion batteries, the main issue that is faced is the larger 'ionic radius' of Na^+(~1.02Å)in contrast with 'ionic radius' of Li^+(~0.76Å). Due to this generally used graphite as anode material for Li-ion battery is not acceptable for Na-ion batteries. Thus, research activity to find an stable anode material for Na-ion battery is widely done.

According to Manoj K. et al.[1]reported that amorphous silicon(a-Si) based anode material can be used for Na-ion batteries. It gives the ways to improve the electrochemical performance of such batteries. Si atom can host upto 0.76 Na corresponding to highest specific capacity of ~725 $mAhg^{-1}$ for $Na_{0.76}Si$.Such lower Na-intake in Si leads to less volume expansion(~114%) than Li-intake(~300%).This might lead to less problems related to stress development, fracture and capacity fade incase of Na-ion batteries as compared to the Li-ion batteries.

Kejie Zhao et.al.[6] predicted that inelastic deformation of silicon electrodes can prevent fracture when feature size is small and yield strength is low in Li-ion batteries.Sindhuja Renganathan et.al [7]indicated that higher stresses are developed and damage is initiated in the particles of negative electrode close to separator. It also shows that the stresses developed in the anode are higher than in the cathode.Yue Qi et.al[8] investigated the ductile and brittle behavior of electrode materials. It says that there is ductile to brittle transition during lithiation of Al but not in Si.Kejie Zhao et.al.[9] formulated a theory which models the lithiation and large elastic plastic deformation. It shows that plastic yielding in electrodes can reduce the magnitude of stress.M. K. Jangid et.al[10]establishes the stability of use of c-Si/a-Si structured nano-wires towards the reversible Na-storage in Si.The Na gets stored in bulk of a-Si shell and not in c-Si core or surface.

The mechanical stress development and fracture with use of a-Si as anode material in Na-ion batteries during repeated sodiation/desodiation cycles is vital factor for performance and durability of such batteries. This issue can be fairly said is yet unexplored. This present study predicts the theoretical stresses during elastic and plastic deformation induced in the a-Si films during sodiation/desodiation cycles.

The relation between State of charge (SOC) and a-Si film thickness during sodium insertion is predicted in current research. This is used for measuring the substrate curvature using Stoney's Equation. The results are used to find out the average stress in the a-Si film during Na insertion as compared to Li insertion.

II. THEORETICAL MODEL

Considering the study ofManoj K. et al.[1] a-Si films are of 50 nm thickness deposited on the copper substrate of 0.025 mm thickness and $4cm^2$ area. The a-Si films on copper are cut into circular discs and assembled against sodium metal in Ar-filled glove box.1M $NaClO_4$ was used as aelectrolyte and glass microfiber filter paper was used as aseparator. Thea-Sielectrodes were sodiated at the rate of C/10 considering

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maximum specific capacity of $725mAg^{-1}$.Fig.1 shows the schematic representation of the a-Si film on the Cu substrate.

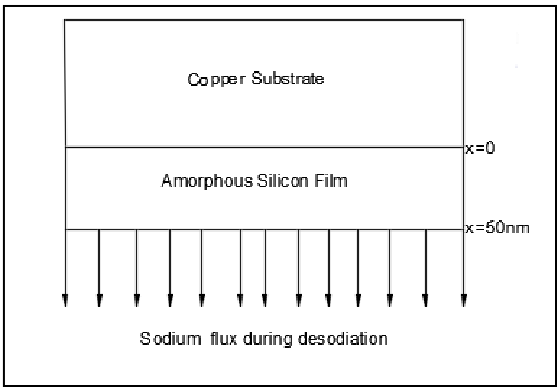

Fig 1:- Schematic representation of the a-Si film on the Cu substrate.

III. THICKNESS OF a-Si THIN FILM

As shown in the Fig. 1, a-Si thin film is constrained in the plane of film by relatively thick Cu substrate. Thus, Na insertion causes the expansion of electrode in thickness direction. Thus, we take thickness of film, t_f, to be linear with SOC or specific capacity.[2]

$$t_f = t_o(1 + \beta s)$$

Where t_o is initial thickness of a-Si film, β is maximum volume expansion when a-Si is fully sodiated (114%) and s is SOC of electrode, value ranging from 0 for pure a-Si to the value 1 representing fully sodiated state (considering $Na_{0.76}Si$ with a capacity of 725 $mAhg^{-1}$,sodiation cycles at the rate of C/10).

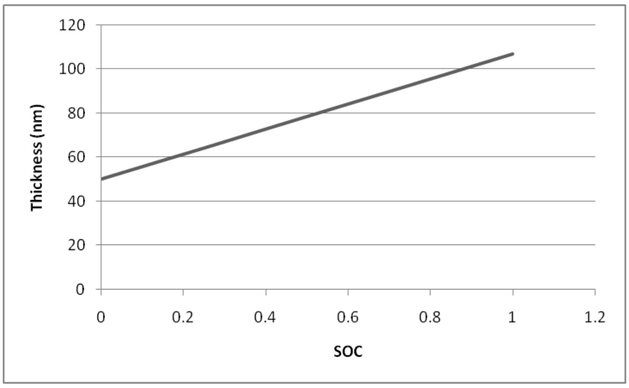

Fig 2:- Thickness of thin film a-Si electrode as a function of SOC/sodiation time at constant charge rate of C/10.

Fig.2. shows thickness of a-Si thin film as function of SOC at the charging rate of C/10.It is seen that due to expansion, the film thickness reaches to maximum of about 107nm during sodiation.

IV. THEORETICAL CALCULATIONS FOR a-Si FILM STRESS

Stress development in a-Si films during sodiation and desodiation was calculated from substrate curvature and Stoney's Equation.

The thickness of film t_f is very thin as compared to the thickness of Cu substrate t_s. The film undergoes elastic mismatch strain with respect to the substrate due to thermal expansion effects, phase transformation, chemical reaction or other physical effect[3]. The stress associated with the mismatch strain causes curvature of substrate. The goal is to find this substrate curvature. It is assumed that the strain is isotropic tension or compression in plane of film and the substrate is taken to be isotropic elastic solid with elastic modulus E_s=130GPa, poison's ratio μ_s=0.34[3]. The subscript's' is used to denote properties of Cu substrate and 'f' is used for a-Si film.

The substrate deformation is calculated using the following theory. The substrate is initially separate from thin film, stress free and undeformed.The force f with the dimensions of force per unit length is induced in the film by external means. This induces elastic mismatch strain and corresponding stress in the free film. The strained film is then brought into contact with substrate surface and bonded to it. The external means of strained film is relaxed due to which, there is deformation in the substrate.

Substrate curvature(k) is given by the following formula:-

$$k = \frac{6\sigma_m t_f}{M_s t_s^2}$$

Where, σ_m is mismatch stress at temperature of 172° [4], M_s is bi-axial modulus of substrate, t_s is thickness of substrate,

$$M_s = \frac{E_s}{1 - \mu_s}$$

For the tensile stress the substrate bonded to the film becomes concave and for compressive stress, the substrate becomes convex.

The average stress developed in the film is deduced from the substrate curvature using Stoney's Equation.

$$\sigma_f = \sigma_r + \frac{E_s t_s^2 k}{6t_f(1 - \mu_s)}$$

Where, σ_f is average stress in film and $\sigma_r$is residual stress.

Fig.3. shows stress in the a-Si film as a function of capacity. Upon sodiation the substrate prevents in-plane expansion of film which leads to compression and increases linearly with capacity. This indicates elastic response in the film. At compressive stress of about 1.04 GPa, the film appears to reach elastic limit and begins to flow plastically with further sodiation to accommodate additional volume expansion. The stress decreases with sodiation reaching value of about 0.8 GPa. Thus, it can be concluded that stress of sodiated a-Si decreases as Na concentration increases.

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Upon desodiation, the unloading is elastic; the stress reverses in tension to about 0.94 GPa where the film flows plastically in tension to accommodate reduction in volume. Finally, the stress increases to about 1.1GPa.

Note that, the stress response is same during sodiation and desodiation at any state of charge i.e. the stress is almost similar in compression and tension. Thus, the film experiences repeated tensile and compressive plastic flow during desodiation and sodiation process respectively. It is observed that the elastic plastic response during sodiation/desodiation cycles is similar to the lithiation/delithiation cycles in Li-ion batteries. The magnitude of stress is less during Na insertion/removal in a-Si (~1.1GPa) than during Li insertion/removal in a-Si (~1.75GPa)[5].Thus we can say that the calculated values can be used for further design and development of the Na-ion batteries.

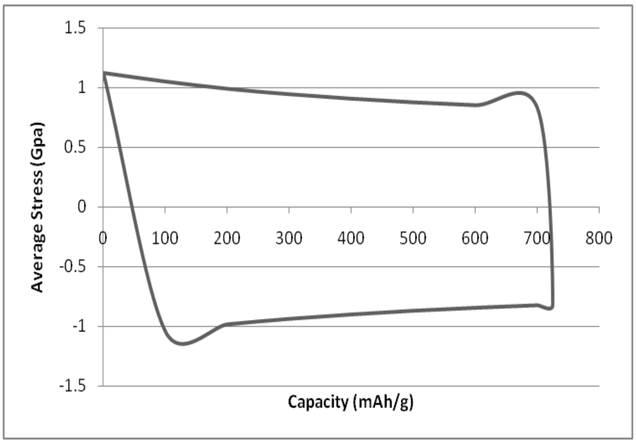

Fig 3:- Average stresses in a-Si electrode during sodiation /desodiation.

V. CONCLUSION

This paper calculates the average stresses induced in the a-Si when used as alloying reaction based anode material for Na-ion batteries. The elastic stress noted during sodiation/desodiation response is about 1.1GPa which is comparatively less with the elastic stress recorded during lithiation/delithiation (1.75GPa).Thus we can say that the calculated values can be used for further design and development of the upcoming Na-ion batteries. The fracture energy and elastic modulus of sodiated thin film silicon electrodes at various sodium concentrations can be measured as a future scope after this research. Also acomputational model for large plastic deformation of anode electrodes in Na-ion batteries can be developed

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