Project Title:	Role of layered 2D layered materials (graphene, MoS_2) and shape memory alloy as buffer interlayers for improving cyclic stability of electrode materials for Li and Na-ion batteries
Project Number	**IMURA0640**

Monash Main Supervisor (Name, Email Id, Phone)	Dr. Nikhil Medhekar ; e-mail: Nikhil.Medhekar@monash.edu ;	*Full name, Email*
Monash Co-supervisor(s) (Name, Email Id, Phone)		
Monash Department:	Materials Science and Engineering	
Monash ADRT (Name,Email)	Emaanuele Viterbo	*Full name, email*
IITB Main Supervisor (Name, Email Id, Phone)	Dr. Amartya Mukhopadhyay ; e-mail: amartya_mukhopadhyay@iitb.ac.in ;	*Full name, Email*
IITB Co-supervisor(s) (Name, Email Id, Phone)	Dr. M. Aslam e-mail: aslam@phy.iitb.ac.in	
IITB Department:	Metallurgical Engineering and Materials Science (for main supervisor); Physics (for co-supervisor)	

Research Academy Themes:

Highlight which of the Academy's Theme(s) this project will address?

(*Feel free to nominate more than one. For more information, see www.iitbmonash.org)*

1. Advanced computational engineering, simulation and manufacture

3. Clean Energy

5. Nanotechnology

The research problem

Anode materials in advanced rechargeable batteries (such as Li-ion and Na-ion batteries) operating based on reversible alloying/dealloying with Li or Na (such as Si, Sn etc.) possessing theoretical capacity higher than that of graphitic carbon by up to even an order of magnitude, along with improved safety aspects. However, huge volumetric changes during Li/Na-insertion/removal (> 300% upon full lithiation) lead to severe stress developments, concomitant fracture/disintegration and loss of contact with current collector [1-4]. This not only leads to drastic capacity fade upon electrochemical cycling in its pristine form, but also results in continued formation of SEI layer due to repeated exposure of fresh (fractured) surfaces to the electrolyte. Such phenomenon causes significant irreversible capacity losses (lower coulombic efficiency) even well past the first few cycles. Stress development has also been reported to negatively affect the overall thermodynamics of Li-insertion/removal, along with rate capability and actually achievable Li-capacity, especially during the lithiation half cycle [1,5]. One of the avenues to minimize the stress related degradations is insertion of a buffer layer between the active materials (say Si, Sn etc.) and the current collector. In this context, research efforts [1,6-8] over the last few years have indicated possible beneficial effects of using layered materials such as graphenic carbon (including multi-layered graphene) and shape memory alloys (such as NiTi) as the buffer interlayer. The possible uses of other layered materials such as MoS_2 to such effects are yet to be investigated. While the shape memory alloys are expected to lead to buffering of the stress development via reversible 'super-elastic' behavior, the layered 2D materials (like few layers graphene and MoS_2) possess capabilities related to reversible sliding of layers, greater specific surface area and efficient charge transfer. Accordingly, effective and optimized usages of the same as interlayers/buffers are expected to render the successful usage of the high capacity alloy anode materials (which otherwise suffer drastically from the stress related issues, as above).

However, to-date there has been no report on investigation related to experimental determinations of the stress developments of such electrode materials in the presence of such 'buffer layer', in comparison to those in the absence of the same. Furthermore, still lacking is any systematic investigation and understanding on the possible effects of the interface properties on the integrities of the alloy anodes (pristine and in composite form upon insertion of buffer layer) at the various stages of lithiation delithiation.

References

1. A. Mukhopadhyay, B. W. Sheldon; Deformation and stress in electrode materials for Li-ion batteries. *Prog. Mater. Sci.* **63** (2014) 58.
2. A. Mukhopadhyay, R. Kali, S. Badjate, A. Tokranov, B. W. Sheldon; Plastic deformation associated with phase transformations during lithiation/delithiation of Sn. *Scripta. Mater.* **92** (2014) 47.
3. J. O. Besenhard, J. Yang, M. Winter; Will advanced lithium-alloy anodes have a chance in lithium-ion batteries? *J. Power Sources* **68** (1997) 87.
4. M. Mortazavi, J. Deng. V. B. Shenoy and N. V. Medhekar; Elastic softening of alloy negative electrodes for Na-ion batteries. *J. Power Sources* **225** (2013) 207.
5. V. A. Sethuraman, V. Srinivasan, A. F. Bower, P. R. Guduru; In-situ Measurements of stress-potential coupling in lithiated silicon. *J. Electrochem. Soc.* **157** (2010) A1253.
6. M. L. Terranova, S. Orlanducci, E. Tamburri, V. Guglielmotti, M. Rossi; Si/C hybrid nanostructures for Li-ion anodes: An overview. *J. Power Sources* **246** (2014) 167.
7. R. Epur, M. K. Datta, P. N. Kumta; Nanoscale engineered electrochemically active silicon–CNT heterostructures-novel anodes for Li-ion application. *Electrochim. Acta* **85** (2012) 680.
8. R. Hu, M. Zhu, H. Wang, J. Liu, O. Liuzhang, J. Zou; Sn buffered by shape memory effect of NiTi alloys as high-performance anodes for lithium ion batteries. *Acta Mater.* **60** (2012) 4695.

Project aims

Against these backdrops, as part of the proposed work, attempts will be made to develop better insights into the possible role of buffer materials (such as few/multi-layered graphene, thicker graphite, MoS_2 and shape memory alloys like NiTi) and the corresponding interfaces on the electrochemical behaviour, stress development and cyclic stability of the alloying reaction based anode materials (such as a-Si, Sn etc.). In the proposed investigations, model electrode material/architecture comprised of continuous (and later patterned) films of active materials deposited on fairly well-ordered graphene/graphite films, MoS_2 films or NiTi films will be used.

Using such relatively simple architecture, monitoring of the stress developments will be performed *in-situ* during electrochemical cycling in the presence and absence of the buffer interlayers for the first time (to be performed at IIT Bombay). It is to be noted that, to the best of the PI's knowledge, such innovative technique/expertise to monitor the stress development in electrode materials in real-time during electrochemical cycling is, as of now, available only in the PI's group in India (and only a very few groups worldwide) [1-6]. Additionally, to further elucidate/understand the possible roles of buffer materials and the interfaces, systematic studies concerning adhesion strengths and mechanical integrities of the film electrodes at various stages of the electrochemical cycling will also be performed (to be performed at IIT Bombay). More detailed understandings of the relevant properties of the interfaces between the active materials, buffer interlayers and the current collector at the various states of charges and stages of electrochemical cycling will be obtained via simulation (molecular dynamics and DFT; to be performed at Monash University).

References

1. F. J. Sonia, B. Ananthoju, M. K. Jangid, R. Kali, M. Aslam, A. Mukhopadhyay; Insight into the mechanical integrity of few layers graphene upon lithiation/delithiation via *in-situ* monitoring of stress development. *Carbon* **88** (2015) 206
2. A. Mukhopadhyay, R. Kali, S. Badjate, A. Tokranov, B. W. Sheldon; Plastic deformation associated with phase

transformations during lithiation/delithiation of Sn. *Scripta. Mater.* **92** (2014) 47.
3. A. Mukhopadhyay, A. Tokranov, X. Xiao, B. W. Sheldon; Stress Development due to Surface Processes in Graphite Electrodes for Li-ion batteries: A first report. *Electrochim. Acta.* **66** (2012) 28
4. A. Tokranov, B. W. Sheldon, P. Lu, X. Xiao, A. Mukhopadhyay; The Origin of Stress in the Solid Electrolyte Interphase on Carbon Electrodes for Li-ion Batteries; *J. Electrochem. Soc.* **161** (2014) A58
5. A. Mukhopadhyay, A. Tokranov, F. Guo, X. Xiao, R. H. Hurt, B. W. Sheldon; Engineering of graphene layer orientation to attain high rate capability and anisotropic properties. *Adv. Funct. Mater.* **23** (2013) 2397
6. V. Malav, M. K Jangid, I. Hait, A. Mukhopadhyay; In-situ monitoring of stress developments and mechanical integrity during galvanostatic cycling of $LiCoO_2$ thin films; *ECS Electrochem. lett.* **4** (2015) A148

Expected outcomes

The project aims at evaluating and understanding the roles and effects of the presence/types of ‘buffer’ interlayers on the mechanical integrity and concomitant cyclic stability of metallic anode materials having varied dimensions for Li/Na-ion batteries.

The innovative and systematic electrochemical-mechanical *in-situ* studies, along with in-depth studies related to properties of the interfaces (including simulation) will help elucidate the effects of such interlayers, especially their properties and interfacial properties on the aspects related to cyclic stability of such electrode materials.

The information concerning the required/beneficial properties of the ‘buffer’ materials and the interfaces and the dimensions of the active materials suitable for enhanced cyclic stability will aid in the practical development of high performance electrodes (possessing significantly improved cycle life) based on such high capacity and safer anode materials.

On a more general note, the results and understandings developed on the basis of the proposed project will contribute immensely towards allowing successful usage of the high capacity alloy anode materials, which otherwise suffer drastically from stress related degradation and capacity fade. This will lead to the development of electrochemical energy storage systems possessing significantly enhanced energy densities, safety and cycle life (the need of the day).

How will the project address the Goals of the above Themes?

In a broader perspective, the presently proposed project is based on application of **nanomaterials** (such as thin films, layered 2D materials like graphene, MoS_2) and **nanotechnology** (such as development of multi-layered thin films, electrochemical-mechanical *in-situ* studies with nanostructured materials and interfaces etc.) towards improvements in the electrochemical **energy storage** technology. Such concerned improvements (based on the overall objective of the project) are essential for rendering the energy storage technologies suitable for applications in *electric vehicles* (which is needed for *controlling environmental pollution* and also in light of the *depletion of fossil fuels*) and *grid energy storage* (which is needed for allowing the large scale usage of the *cleaner*, but intermittent, *renewable sources of energy* like solar and wind). Finally, a key aspect of this project is to investigate the atomic structure and stress generation mechanisms of the interfaces using density functional theory or molecular dynamics simulations. These methods quire state-of-art massively parallel high performance computing systems, consequently addressing the theme of **advanced computational engineering**.

Capabilities and Degrees Required

The student should ideally have a basic degree in areas related to Metallurgical Engineering (including Ceramic Engineering) and/or Materials Science. Students having degree in Physics will also be considered. Candidates having a CPI of > 8/10 or overall % of 80% in the qualifying examination might get preference. Similarly, candidates having some previous research experience during Master’s program or as research/project associate might get preference.

Potential Collaborators

Prof. Prita Pant (Metallurgical Engineering and Materials Science, IIT Bombay), Prof. Sagar Mitra (Energy Science and Engineering, IIT Bombay), Prof. Douglas R. MacFarlane (School of Chemistry, Monash), Prof. Yu Lin Zhong (Materials Science and Engineering, Monash)

Please provide a few key words relating to this project to make it easier for the students to apply.

nanomaterials for energy storage, layered 2D materials (like graphene, MoS_2), electrode materials, electrochemical-mechanical *in-situ* studies, multi-layered films, simulation and modelling, buffer material, interface, mechanical integrity, electrochemical cycling stability