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Guar gum: Structural and electrochemical characterization of natural polymer based binder for silicon–carbon composite rechargeable Li-ion battery anodes

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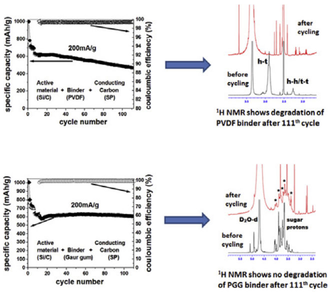
HIGHLIGHTS

- Cyclability of Si/C composite was studied with different polymeric binders.
- Si/C composite exhibit reversible capacity of ~780 mAh/g at ~50 mA/g (C/16) rate.
- PVDF and PGG binders were selected with elastic moduli of ~1000 MPa and ~3200 MPa, respectively.
- Higher elastic modulus PGG binder shows better long term cyclability compared to PVDF binder.
- ^{1}H-NMR shows structural degradation of PVDF, whereas PGG shows structural integrity beyond 100 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Long term cyclability of a composite Li-ion anode electrode comprised of 82 wt.% Si/C lithium ion active material along with 8 wt.% polymeric binder and 10 wt.% Super P conductive carbon black has been studied utilizing polymeric binders exhibiting different elastic/tensile moduli and tensile yield strengths. Accordingly, electrochemically active Si/C composite synthesized by high energy mechanical milling (HEMM), exhibiting reversible specific capacities of ~780 mAh/g and ~600 mAh/g at charge/discharge rates of ~50 mA/g and ~200 mA/g, respectively were selected as the Li-ion active anode. Polyvinylidene fluoride (PVDF) and purified guar gum (PGG) with reported elastic moduli ~1000 MPa and ~3200 MPa, respectively were selected as the binders. Results show that the composite electrode (Si/C + binder + conducting carbon) comprising the higher elastic modulus binder (PGG) exhibits better long term cyclability contrasted with PVDF. ^{1}H-NMR analysis of the polymer before and after cycling shows structural degradation/deformation of the low elastic modulus PVDF, whereas the high elastic modulus PGG binder shows no permanent structural deformation or damage. The results presented herein thus suggest that PGG based polymers exhibiting high elastic modulus are a promising class of

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binders with the desired mechanical integrity needed for enduring the colossal volume expansion stresses of Si/C based composite anodes.

1. Introduction

Rechargeable Li-ion battery (LIB) technology is considered as the frontrunner amongst various electrochemical energy storage (EES) devices due to its high usable specific energy (~100–200 Wh/kg) and high operating (~3 V–5 V) voltage window [1,2]. Despite considerable advancements, systems meeting the higher energy demand applications are still elusive for complete deployment in plug-in electric vehicles (PEV) or electric vehicles (EV) systems due to the limited energy and power densities [1–4]. In order to further improve the energy density of LIBs to render them amenable for higher energy application (≥300 Wh/kg), alternative Si based anode materials with an attractive theoretical specific capacity ~4200 mA/g representing a ~10-fold increment over the traditionally used graphite anode has been extensively studied in recent years [1,3,5–11]. The ubiquitous structural disintegration of Si during repeated alloying/de-alloying following colossal volume expansion (~300%), and the resultant capacity fade within few tenths of cycles is universally reported [12–15]. In order to improve the structural stability/integrity as well as the long term cyclability of Si based anodes, nanotechnology and nanoscale architectures have been explored over the past several years for generating various nanoscale morphologies of Si (*e.g.* nanotube, nanowire, nano-droplet) and nano-composites of Si and C (*e.g.* Si/C nanocomposite) [1,5–19]. Despite much advances, Si based nanomaterials or nano-composite electrodes still display structural degradation and limited cyclability with a fade in capacity exceeding 0.1% per cycle.

Concomitant with the materials development work, there are also several published reports demonstrating improvement in the cyclability of Si based active materials by proper design and effective development of composite electrode (active materials + binder + conducting carbon) exploiting the mechanical properties of the binder combined with effective interactions of the binder functional groups with the native silicon oxide layers inherent on the Si surfaces [20–26]. Consequently, during the electrode manufacturing process, a small volume faction of inactive binder (~2–8 wt.%), facilitating uniform binding of the particles is homogeneously mixed with micron sized electro-active particles (<40 μm) along with electronically conductive carbon (CC) (*e.g.* Super P carbon black) to yield a homogeneous slurry. The slurry is then cast onto suitable current collectors of few microns thick to form a particulate composite electrode. The particulate composite electrode generated on a suitable current collector must be structurally and chemically stable during repeated cycling of the electrode for at least a thousand or greater cycles. In the case of the widely used graphitic anode deployed in commercial LIBs, the composite electrode utilize PVDF as a binder displaying excellent cyclability during the charge/discharge processes [27,28].

The mechanical stress/strain generated on graphite as well as the electrode during alloying and dealloying processes with Li-ion (~10% volume change) is expected fortuitously to lie within the elastic limit of graphite and the composite electrode. Hence the systems do not exhibit any permanent deformation or mechanical degradation of graphite or the intercalated LiC_6 phase [27,28]. However, it is well-known that PVDF commonly used in commercial graphitic anodes, is not suitable for Si based active materials [20–26,29,30]. The tremendous mechanical stress/strain beyond the elastic limit generated within the composite electrode (Si + binder + CC) results inevitably in volume expansion related failure of Si based composite electrode causing the well-known mechanical degradation or permanent deformation of the composite electrode leading to loss of contact between the active material with the current collector causing capacity loss in within few tenths of cycles.

Improvement in cycling of Si based composite electrode clearly requires indigenous engineering of the mechanical properties of the composite electrode to achieve optimum elastic modulus, strength and toughness, and low stress/strain profile on the composite electrode (within the elastic limit) by proper distribution of the generated stress/strain within the composite electrode. It is well known that the mechanical properties (*e.g.* elastic modulus, fracture strength) of the particulate composite electrode and stress/strain distribution within the composite electrode depend on the mechanical properties, which in turn depend on the volume fraction of the binder matrix as well as the dispersed active particles following the Halpin–Tsai equation [31]. In this regard, stiffer (high elastic modulus) binders such as water soluble Na-Carboxymethyl cellulose (Na-CMC), polyacrylic acid (PAA), sodium alginate based binder and different blended polymers have been recently identified as better choices compared to PVDF for Si based system. However, despite the novelty and improved initial performance, they all exhibit degradation over several cycles [20–26,29,30] casting doubts on their efficacy for long term performance. In the present investigation novel water soluble, biodegradable, non-toxic and good film forming ability of polysaccharide based binders namely, purified guar gum (PGG) obtained after purification of raw guar gum has been studied as a potential binder system for the Si/C nanocomposite electrode system. The biodegradable nature of the system further adds to the possibility of green engineering design and the environmentally benign aspect of polymeric binder systems for LIB.

Guar gum is a natural nonionic polysaccharide extracted from the refined endosperm of cluster bean seeds, chemically classified as galactomannan. It is basically composed of a straight chain backbone of D-mannose units, united by β (1–4) glycoside linkages, and bears a single D-galactose side chain unit on approximately every alternate mannose, joined to it by an α (1–6) glycoside linkage (see Fig. 1) [32,33] making it an attractive system for exploring as a binder for LIBs as indicated in the present study. In recent publications, gaur gum and its derivative has been reported as a suitable binder for silicon nanoparticles which shows excellent electrochemical performance [34,35]. In the present study, contrary with the published reports however, Si/C composite consisting of more ubiquitous micron-sized Si dispersed on graphite matrix obtained by cost effective high energy ball milling has been used as a Li-ion active material to study the cyclability of the composite electrode (Si + binder + CC) based on PGG binder and Si/C active materials. In addition, a fundamental study of the change in molecular structure of the binder during Li-ion cycling determined by proton nuclear magnetic resonance (^{1}H-NMR) of PGG along with PVDF before and after electrochemical cycling has been reported in this article. The Si/C Li-ion active materials, synthesized by high energy mechanical milling (HEMM) as reported by the present