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A high-rate germanium-particle slurry cast Li-ion anode with high Coulombic efficiency and long cycle life

Kyle C. Klavetter [a,c], Sean M. Wood [a,c], Yong-Mao Lin [a,c], Jonathan L. Snider [a,c], Nicholas C. Davy [a,c], Aaron M. Chockla [a,c], Dwight K. Romanovicz [e], Brian A. Korgel [a,c,d], Joo-Woon Lee [a,c,f], Adam Heller [a,c], C. Buddie Mullins [a,b,c,d,*]

[a] Department of Chemical Engineering, University of Texas at Austin, 1 University Station, C0400 Austin, TX 78712-0231, United States
[b] Department Chemistry and Biochemistry, University of Texas at Austin, 1 University Station, C0400 Austin, TX 78712-0231, United States
[c] Center for Electrochemistry, University of Texas at Austin, 1 University Station, C0400 Austin, TX 78712-0231, United States
[d] Texas Materials Institute, and Center for Nano and Molecular Science, University of Texas at Austin, 1 University Station, C0400 Austin, TX 78712-0231, United States
[e] ICMB Core Lab, University of Texas at Austin, 1 University Station, C0400 Austin, TX 78712-0231, United States
[f] School of Liberal Arts & Sciences, Korea National University of Transportation, Chungju, Chungbuk 380-702, South Korea

HIGHLIGHTS

- ► Ge-based slurry cast Li-ion anode performs stably at high C-rates for 2500 cycles.
- ► Fluoroethylene carbonate (FEC) based electrolyte critical to anode performance.
- ► Stable performance and near 100% Coulombic efficiency at 10*C* for 500 cycles.
- ► d*q*/d*V* show thermodynamic reversibility of FEC- but not EC-based electrode.
- ► Cross-sectional TEM with SEM show structure of cycled anode and SEI.

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ABSTRACT

We report stable, high capacity cycling performance over 2500 deep cycles at variable *C*-rates (1*C*, 5*C* and 10*C*) for slurry-cast Li-ion battery anodes made using commercially-available germanium nanopowder. The determining factor in cycling performance was the use of fluoroethylene carbonate (FEC) rather than ethylene carbonate (EC) as a co-solvent in the electrolyte. Cycling tests for the FEC-based electrode showed stable performance close to 700 mAh g^{-1} through 500 cycles at 10*C* with near 100% Coulombic efficiency. These results show that a Ge-based slurry-cast electrode using active material structured only as a simple particle can be used to create an electrode system which is a candidate for optimization and scale-up. These cycling improvements obtained using the FEC-based electrolyte complements recent progress in Ge-based electrode research which has focused on improving performance through tailored structural and chemical modifications to the active material structure. The effect of the electrolyte on Li-ion transport, electrode stability toward oxidation, and electrode and SEI structural stability was studied using electrochemical impedance spectroscopy, differential capacity profiles, SEM and cross-sectional TEM imaging where we characterize the evolution of the electrode structure cycled with the FEC-based electrolyte considering the type and extent of SEI growth, particle agglomeration and fracturing.

1. Introduction

High-power and energy-dense lithium-ion batteries are desired for portable electronics and wide-spread adoption to power electric vehicles. [1] Transitioning from the commercially-used graphite carbon anode (372 mAh g^{-1}) to metallic silicon, germanium, or various metal oxides could theoretically increase the anode capacity by up to an order of magnitude. However, these electrode materials commonly show capacity fade and inadequate Coulombic efficiencies, particularly at high current densities.

Ge has attracted attention as an alternative anode material because of its large theoretical capacity (1384 mAh g^{-1} or

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* Corresponding author. Department of Chemical Engineering, University of Texas at Austin, 1 University Station, C0400 Austin, TX 78712-0231, United States.
E-mail address: mullins@che.utexas.edu (C.B. Mullins).

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7366 mAh cm^{-3} corresponding to Li$_{15}$Ge$_4$), [2,3] high electrical conductivity (10^4 times higher than in silicon) [4,5] and exceptional Li$^+$ ion diffusivity (400 times greater than in silicon at room temperature) [5,6]. Although Ge is about as abundant as tin, there are no concentrated germanium ores and there is very little demand for germanium; for these reasons its price is presently excessive for use in vehicular applications, but applications might be found for mobile electronics requiring long-lasting, energy-dense and high-power batteries.

As in the case of silicon, the repeated volume change in germanium (230%) [5] transitioning to its fully lithiated phase results in large strain gradients that may lead to the cracking and pulverization of particles and the exfoliation of the anode film from the current collector [7,8]. Freshly-exposed fractured surfaces are coated by reduced electrolyte solvents that decompose to form an electrically insulating solid electrolyte interphase (SEI) through irreversible reactions with Li, resulting in both diminished Coulombic efficiency and capacity fade due to slowed Li-ion transport through the surface film and the electrical isolation of fractured material [9–11]. At high current densities, the effects of mechanical strain are more pronounced, leading to poor cycle life as a consequence of particle fracture [5] and a dynamic, continually degrading and reforming SEI resulting from the instability of the Ge-organic electrolyte interface induced by the particle volume changes [12,13].

Nanostructured germanium morphologies for thin films [5,14], nanoparticles [15,16], nanowires [17,18], nanotubes [7], nanocomposites [19,20] and nanocomposite-carbon matrices [21,22] have been investigated in part because small grained materials are known to superplastically deform to accommodate greater than 200% elongation [23–25]. An *in situ* TEM study by Liu et al. showed the mechanical robustness of germanium nanowires (40–125 nm diameter) reversibly cycled between bulk germanium and Li$_{15}$Ge$_4$ in under 1 min [3]. The nanoscale morphologies better accommodate high strain [26,27], provide shorter Li diffusion distances [28,29] and, as has been demonstrated recently for some Si-based anode designs [30–35], may lead to a more stable SEI/active–material interface.

Advances in the design of germanium anode materials through attention to decreasing Li-ion diffusion distances and improving the structural stability of the particle and SEI have led to exceptional high-rate performance in thin film electrodes [5,14,26,36,37] and more recently to potentially manufacturable slurry cast films [7,16–18,38]. For example, Cho and co-workers reported high rate capacity, slurry cast germanium anodes with stable performance at high rates for up to many hundreds of cycles by using novel nanotube, [7] honeycomb [16] and nanostructured clustered germanium/carbon morphologies [38]. In these electrodes, the Ge particles used were specifically designed for fast Li diffusion and, moreover, were partially or fully shielded from contact with the electrolyte or designed to allow for volumetric expansion away from the SEI into empty space. For the nanostructured clustered germanium/carbon morphologies, after capacity fade from an initial capacity close to 1200 mAh g^{-1}, a stable specific capacity of 360 mAh g^{-1} was reached after 100 cycles at 40*C* (64 A g^{-1}) [38] and minimal capacity fade was observed for 400 cycles at 0.3/0.6*C* (0.5/1.0 A g^{-1}) lithiation/delithiation rates [7].

Recently, Chockla et al. reported an alternative means to improving the SEI/particle interface stability by using fluorinated ethylene carbonate (FEC) based electrolytes for a slurry cast germanium nanowire-based electrode to achieve stable cycling performance [39]. Here we expand upon this work and similar research into the use of FEC for Si-based electrodes [40–43], studying the evolution of the Ge/EC-based and Ge/FEC-based electrode systems through many cycles with electrochemical testing and detailed study of the electrode architecture by SEM and TEM to demonstrate the effectiveness of the FEC-based electrolyte.

Without the mechanical advantages and short Li-diffusion distances of nanowires as an active material like those used by Chockla et al., and without the improved SEI stability that might otherwise be obtained by using Ge nanostructures intentionally designed to address the repetitive volumetric expansions and contractions that continuously degrade the Ge nanoparticle/SEI interface, [34] we report much improved electrode performance, with higher capacity, Coulombic efficiency and specific power output over longer cycle lifetimes for a slurry cast Ge-based electrode. Made with polydisperse, untailored, commercially-scalable Ge nanopowder and using a FEC-based rather than EC-based electrolyte, the electrode described herein achieves stable performance throughout a 2500 cycle variable, high *C*-rate test (through nine, successive 200-cycle iterations at 1*C*, 5*C* and 10*C* followed by 700 cycles at 1*C*, $C = 1.624$ Ah g^{-1}) and a capacity near 700 mAh g^{-1} at 10*C* rate with an average Coulombic efficiency near 100% through 500 cycles. Capacities over 1000 mAh g^{-1} were observed when discharging the electrode at up to 20*C* while charging at 1*C* and a capacity of 425 mAh g^{-1} was achieved for a discharge rate of 50*C*. These results complement the recent progress in slurry cast Ge-based electrode research which has focused on improving cycling performance through structural and chemical modifications to the active material. The notable cycling stability of the electrode in FEC-electrolyte, sustained through both extended cycling and high *C*-rate testing, indicates that the improved performance may be found in the role of FEC forming a SEI that better protects the Ge nanoparticle active material from contact with the electrolyte, a consequence of the different surface films likely rich in lithium fluoride, alkoxy and polycarbonate species which have been found to be the result of FEC reduction [42,44]. This results in higher CE as a consequence of a more stable SEI/particle interface, and, from considering the evolution of the electrode differential capacity profiles, an enhanced stability toward oxidation that significantly delays capacity fade and corresponding oxidation of the Ge nanoparticle active material, a finding analogous to the result recently reported by Etacheri et al. in their study on FEC and Si NW [44]. Herein we report how the FEC-based electrolyte with a Ge-based electrode is an effective means to improving the SEI so as to minimize irreversible losses and better protect the Ge nanoparticle from oxidation, thereby improving the battery performance parameters of interest: long cycle life, specific capacity, capacity retention, Coulombic efficiency and high *C*-rate capability.

2. Experimental

2.1. Ge nanoparticle electrode preparation and battery assembly

Ge nanoparticles (99.9%, American Elements) were used as the active material in the electrode. The reported average particle size was 70–120 nm. However, the actual particle size distribution ranged up to several microns (a typical TEM of Ge particles after dispersing via bath sonication is shown in Supplementary Information Figure SI.1). Slurries of 40:20:40 w/w/w Ge nanoparticles:poly-acrylic acid binder (PAA-450 kDA, Sigma):Super-P Li conductive additive (Timcal) with ethanol as solvent were cast on a copper foil current collector to prepare the electrode for battery testing. This film composition, made of a high weight fraction of conductive additive, was selected to diminish the effect on cycling performance of losing a sustained electrical percolating network as a consequence of particle shifting due to the volumetric expansion and contraction of the Ge nanoparticles during cycling after preliminary screening for slurry compositions with a film composed of 80:10:10 w/w/w (Ge nanoparticles:PAA-450 kDA:Super-P Li conductive additive) showed capacity fade after only 100 cycles at a rate of 1*C*: 0.49 mAh g^{-1} (or 0.05%) capacity fade per cycle with an areal capacity