Germanium as negative electrode material for sodium-ion batteries

Loïc Baggetto [a,*], Jong K. Keum [b], James F. Browning [c], Gabriel M. Veith [a,*]

[a] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[b] Neutron Science Directorate, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[c] Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ARTICLE INFO

ABSTRACT

Germanium thin film electrodes show a reversible Na-ion reaction at potentials around 0.15/0.6 V. The reaction is accompanied with a reversible capacity close to 350 mAh g^{-1}, which matches the value expected for the formation of NaGe. The electrode capacity retention is stable over 15 cycles but subsequently declines. However, using fluoroethylene carbonate (FEC) electrolyte additive positively improves capacity retention and promotes the formation of a thinner SEI. Mechanical degradation due to repeated expansion/shrinkage coupled with SEI formation are the main sources of capacity decline. Preliminary XRD results do not reveal the formation of crystalline phases at full (dis)charge. The excellent charge rate up to 340 C highlights the high potential of nanosized germanium as Na-ion anode.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Alternative energy storage technologies to lithium-ion batteries have drawn significant attention recently, with notable recent advances in Na-ion chemistries [1]. The Na-ion battery system is of particular interest to provide low cost and sustainable energy storage. Numerous studies on suitable cathode materials have been reported [1]; in contrast the chemistries suited to store Na on the anode side have been scarcer but have started to emerge at a fast pace [2–9]. Hard carbons have been reported as possible anode materials with decent storage capacity (~300 mAh g^{-1}), however the material presents relatively limited rate performance and only about half of the electrode capacity can be accessed below 0.5 V vs. Na/Na$^+$ [2].

Density Functional Theory (DFT) calculations predicted the operating voltage of the other group IVa elements Si (954 mAh g^{-1}), Ge (369 mAh g^{-1}), Sn (847 mAh g^{-1}) and Pb (485 mAh g^{-1}), and reported voltage profiles below 0.5 V [3]. The predictions were recalculated for Sn and confirmed experimentally using a wide variety of characterization tools [4]. Sb (660 mAh g^{-1}) has been explored as a potential candidate for Na-ion batteries [5–7]. Intermetallics based on Sb and Sn attract increasing attention, thanks to their potential for better cycle-life and rate performance, as for example for SnSb [8] or Cu$_2$Sb [9]. To date, no studies of the Na-ion reactions of Si and Ge have been reported. For Ge, the electrochemical reaction with Li was explored thoroughly on evaporated and sputtered thin films using in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy

[10,11], and was found to proceed with the reversible formation of an amorphous material of increasing Ge–Ge interatomic distance until the electrode crystallizes into Li$_{15}$Ge$_4$ (1384 mAh g^{-1}).

The present contribution reports for the first time the electrochemical properties of germanium thin film electrodes during Na-ion electrochemical reaction. The reaction potentials obtained with constant current and quasi-equilibrium measurements measured with the galvanostatic intermittent titration technique (GITT) are discussed and compared to former DFT results [3]. Moreover, the performance studied by galvanostatic cycling with(out) FEC electrolyte additive and the (dis)charge rate are presented. Finally, the reaction mechanism studied by XRD for fully (dis)charged electrodes, and failure mechanisms of cycled electrodes examined using scanning electron microscopy (SEM) are discussed.

2. Experimental

Thin film deposition was performed onto roughened Cu foils by DC magnetron sputtering of a N$^+$-doped Ge wafer (Precision Micro-Optics) in an Ar plasma at 30 W and 15 mTorr. Thin films were weighed with μg precision (Mettler MT5 balance) and film thickness was back-calculated based on an expected density of 5.32 g cm^{-3}; for reference a weight of 338 μg represents a thickness of 0.5 μm onto 1.27 cm^2. Electrochemical characterization was conducted at 25 °C with 2-electrode 2032 coin cells prepared inside an Ar-filled glovebox. The cells consisted of pure Na (Sigma-Aldrich) as counter electrode, glass fiber separator impregnated by 1 M NaClO$_4$ in propylene carbonate (Sigma-Aldrich) as electrolyte and Ge as working electrode. When specified, 5 wt.% FEC (Sigma-Aldrich) was used as electrolyte additive.

* Corresponding authors. Tel./fax: +1 865 241 6126.
E-mail addresses: baggettol@ornl.gov (L. Baggetto), veithgm@ornl.gov (G.M. Veith).

Galvanostatic cycling was performed on a Maccor 4000 series. 1 C-rate corresponds to required current to (dis)charge the electrode in 1 h. Rate performance was conducted during discharge (charge) with associated constant-current constant-voltage (CCCV) charge (discharge) steps at 1 C with a current cut-off value of 0.22 (0.17) C. XRD was conducted using a PANalytical X'Pert Pro using Cu-K$_\alpha$ radiation on electrodes sealed with Kapton tape. Charged electrodes rinsed with anhydrous dimethyl carbonate were transferred with minimal air exposure into a Hitachi S-4800 field emission SEM for imaging.

3. Results and discussion

The typical electrochemical response of sputtered Ge thin films is presented in Fig. 1. During the first cycle (Fig. 1a) the discharge comprises a slope with a few small plateaus until a plateau at 0.19 V is reached. We attribute these features to the reduction of surface oxides and the formation of a solid electrolyte interphase (SEI) layer. The rest of the discharge consists of a wide plateau around 0.14 V that is preceded by a potential dip and increase, clearly seen in the derivative plot (inset) as a positive dQ/dV feature, which is typical for the nucleation/growth mechanism of new phases [4,5,10,11]. During charge, the potential rapidly increases to reach a plateau near 0.62 V followed by a slope till 2 V. During the second cycle, the discharge profile starts with a slope and becomes nearly identical to the second part of the first discharge. The potential of the plateau slightly increases to

0.15 V, likely due to an improvement of the reaction kinetics of the charged Ge electrode resulting from the formation of smaller domains, as also found for Sb [5], or due to a different thermodynamic reaction pathway. The reversible storage capacity of these films amounts to about 350 mAh g^{-1} or 0.95 Na/Ge, and may correspond to the formation of an amorphous material with a short range ordering structure close to that of the known NaGe phase [12] of theoretical capacity 369 mAh g^{-1}.

The potential profiles measured using a low current (C/60) and quasi-equilibrium GITT are compared to the voltage prediction of Chevrier and Ceder [3] in Fig. 1b. The voltage obtained by DFT calculations matches fairly well with the average potentials. Using a lower current of C/60 induces only a small difference (~0.01 V) of the plateaus' voltages compared to the values obtained at C/20 (Fig. 1a) with discharge/charge plateaus now measured at 0.16/0.61 V. When the electrode is allowed to rest, the GITT potential approaches more closely the true thermodynamics with the discharge/charge plateaus around 0.28/0.55 V. The larger relaxation of potential during discharge clearly demonstrates that the electrode polarization is larger during the insertion than the removal of Na ions.

The capacity retention of Ge thin film electrodes obtained during galvanostatic cycling is presented in Fig. 1c. The capacity retention of thin electrodes (0.36–0.44 μm) cycled between 0 and 2 V is stable over 15 cycles and declines afterwards independently of the applied current. Cycling between 0 and 1 V slightly improves the capacity
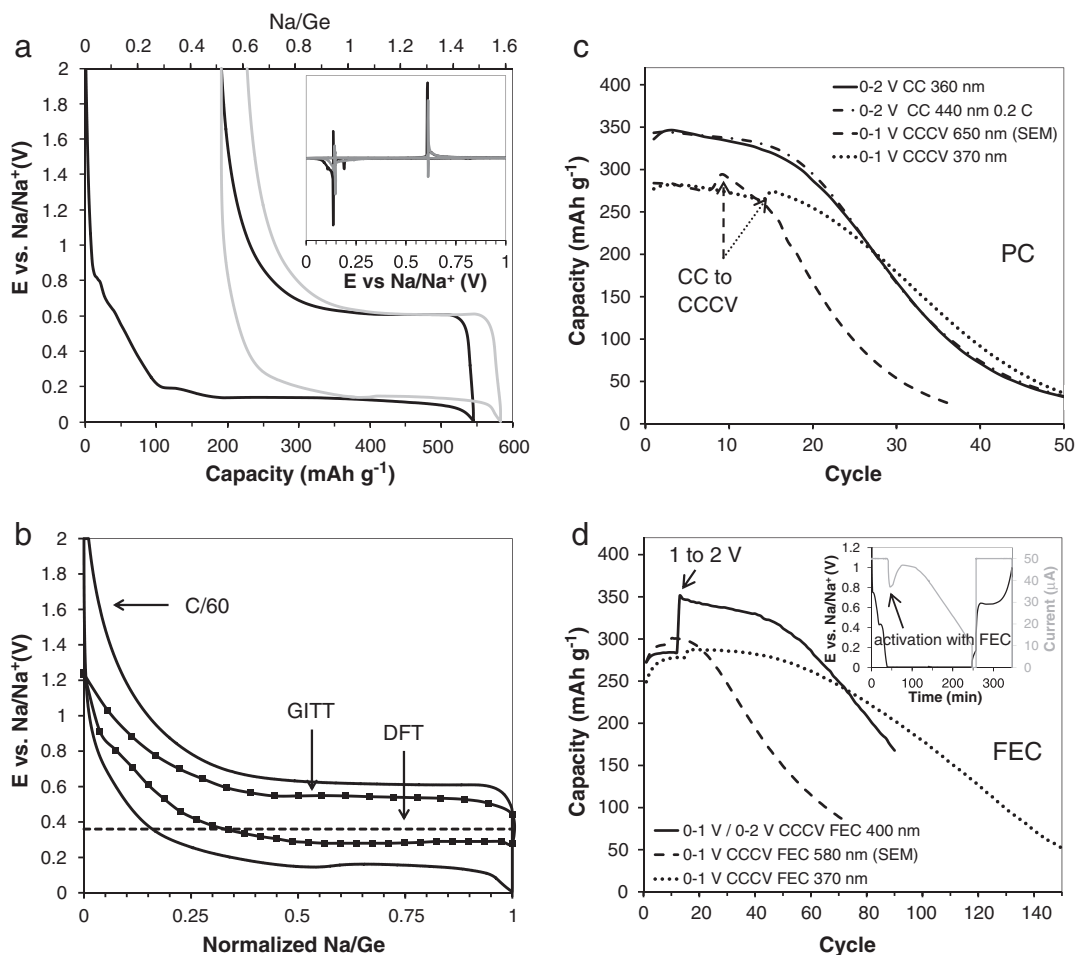
Fig. 1. (a) Typical potential profiles of 0.60 μm thick Ge electrodes during the first two galvanostatic cycles at C/20 from 0.005 to 2 V. The inset shows the corresponding derivative curves. (b) Comparison of the potential profiles obtained at low currents (C/60), during quasi-equilibrium GITT measurements, and predictions by DFT obtained from [3]. Capacity retention of Ge thin film electrodes cycled in (c) PC- and (d) PC/FEC-based electrolytes. Cycling with PC/FEC was conducted using CCCV as activation was necessary during the first discharge (see inset).