Operando Micro-Raman Study Revealing Enhanced Connectivity of Plasmonic Metals Decorated Silicon Anodes for Lithium-Ion Batteries

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ABSTRACT: The efficient formulation of silicon based, high-loading electrode with good capacity retention and cycling stability remains challenging. To gain a better understanding of the ongoing processes and failure mechanisms occurring during battery performance, operando micro-Raman spectroscopy is helpful to map the active silicon sites. Herein, we present the investigation of the electrochemical performance of anodes composed of plasmonic metal (Ag and Au) decorated silicon, designed for enhancing Raman signal. Following the discovery that only a partial amount of the electroactive material undergoes lithiation in the first cycle, we show that the plasmonic metal tips can enhance the connectivity of the Si particles. The micro-Raman mapping of electroactive silicon material reveals how the plasmonic metals influence the distribution of silicon active sites during battery cycling. The ratio of electroactive Si is found to increase from Si to Si/Au and Si/Ag electrodes, and the results are explained in terms of interconnectivity of the particles.

KEYWORDS: operando, Raman spectroscopy, Li-ion battery, galvanic replacement reaction, silicon anode

1. INTRODUCTION

Over the past few decades, the research on rechargeable lithium-ion batteries (LIBs) has mainly focused on their successful utilization in portable electronics, electric vehicles, and long-term energy storage.1−16 However, Li-ion batteries still have not reached the appropriate level of energy storage to fully meet the demands of these applications.17−19 In that regard, silicon (Si) is considered as one of the most promising anode materials for next generation Li-ion batteries, due to its relative abundance and high gravimetric capacity of 3.6 Ah g−1 at very low potentials.1,8−10 Unfortunately, the lithiation of Si during battery cycling is accompanied by large volume expansion of the host material (up to 300%) in the fully lithiated state, which leads to mechanical stress that destroys the electrode and the formation of unstable SEI (solid electrolyte interphase). To overcome these issues, nanostructured, Si based electrode materials such as nanoparticles, nanowires, nanotubes, and nanofibers have been developed, demonstrating improved energy and power densities.10,11−14 However, while high specific capacity could be achieved during cycling, these nanostructured, Si based electrode materials are usually confined to very thin electrodes with very low mass loadings of the active material (<1 mg/cm2).15−17 In addition to using nanostructures, the stability, capacity fading, and loading of the active material may be improved by utilizing nanocomposites such as incorporation of Si into polymers4,10 or carbon15,18 and various metallic nanoparticles.19−21 Furthermore, it has been previously reported that the incorporation of metal nanoparticles into electrode-active materials may improve the capacity and cycling stability of LIBs.22 It is commonly accepted that one of the origins of the LIB failure is the electrical disconnection of the active Si material from the current collector.23 Even though the Coulombic efficiency is very high, the capacity is still fading while working under galvanostatic conditions. Discharge controlled battery cycling may bring a solution to the half-cell issues, but with a nonpractical first charge capacity loss. In other terms, such a strategy will not be applicable in full cell, except for the use of pre-lithiated silicon electrodes which bring issues of safety, since lithiated silicon reacts violently with moisture.

One of the successful routes toward Si anodes was the use of a porous current collector filled with Si nanomaterials.24 Despite the ingenuity of such an approach, the LIB industry still prefers to use slurries for battery processing. For that purpose, the present work describes a “slurry” approach on a Cu current collector. To study the electrochemical lithiation process of Si
nanostructures and understand its failure mechanisms during cycling, a large variety of in situ techniques have been proposed as follows: real-time NMR investigations, operando electron magnetic measurements, and in situ Raman spectroscopy have been introduced. Raman spectroscopy, a powerful, highly specific optical tool, can identify a single molecule and allows scanning and characterization of defined areas in the sample simultaneously. However, since the Raman output signal is relatively weak, surface-enhanced Raman scattering (SERS) is often employed. By introducing noble metals (Ag, Au, or Cu) to the probed material, a large enhancement of the Raman signal may be achieved (order of $10^{10}$). This enhancement occurs due to the localized surface plasmon resonance (LSPR) phenomenon, which arises from the noble metals presence. SERS is very selective and surface-sensitive, by that widening the scope of Raman scattering to include a wide variety of systems, such as the operando analysis of electrochemical, catalytic, biological, and organic structures.

Previous studies demonstrated that micro-Raman is a powerful tool capable of detecting the quality of the connectivity of the silicon particles to the Cu current collector substrate, as well as connectivity of the particles to each other.

Here, we report on the preparation of noble metal decorated Si nanocomposites, by using galvanic replacement reaction (GRR). We have assembled high-loading Si, Si/Ag, and Si/Au anodes in coin cell LIBs and cycled the batteries. The monitoring and mapping of the electrochemically active sites of Si, Si/Ag, and Si/Au nanocomposites with a micro-Raman technique, reveal that the interconnectivity of the electroactive sites of Si has improved, due to the presence of plasmonic metal nanoparticles.

## 2. MATERIALS AND METHODS

Silicon powder (nanocrystalline, average particle size ~ 100 nm (99%, Alfa Aesar)), silver nitrate (AgNO$_3$; 99.9% Ag, Strem Chemicals), hydrogen tetrachloroaurate(III) hydrate (HAuCl$_4$·xH$_2$O (Strem Chemicals), and hydrofluoric acid (HF; Fluka) were used as received.

**Synthesis of Silver–Silicon Composite (Adapted from Reference 41).** A 1.0 g amount of silicon nanopowder was dispersed in 10 mL of absolute ethanol by vigorous stirring. A 1.93 mmol amount of silver nitrate was dissolved in 13.5 mL of absolute ethanol, and 1.5 mL of HF was added while stirring. The solution was then slowly added to the silicon dispersion under magnetic stirring. The mixture was stirred for 3 min and rapidly transferred to the centrifuge (4000 rpm for 5 min) to isolate a deep brown solid. The solid was redispersed in ethanol with a vortex and then centrifuged at 4000 rpm for 5 min to separate the deep brown solid product. The procedure was repeated twice, and the product was dried under vacuum for 8 h at 150 °C to yield a Si/Ag powder.

**Synthesis of Gold–Silicon Composite (Adapted from Reference 41).** A 1.0 g amount of silicon nanopowder was dispersed by magnetic stirring in 10 mL of ethanol. A 0.94 mmol amount of hydrogen tetrachloroaurate(III) hydrate was dissolved in 13.5 mL of absolute ethanol, and 1.5 mL of HF was added while stirring. The solution was then slowly added to the silicon dispersion under magnetic stirring. The mixture was stirred for 3 min and rapidly transferred to the centrifuge (4000 rpm for 5 min) to isolate a deep brown solid. The solid was redispersed in ethanol with a vortex and then centrifuged at 4000 rpm for 5 min to separate the deep brown solid product. The procedure was repeated twice, and the product was dried under vacuum for 8 h at 150 °C to yield a Si/Au powder.

**Characterization.** The morphology of Si/Au and Si/Ag was investigated by transmission electron microscopy (TEM) on a FEI Tecnai-12 instrument operated at 120 kV or a JEOL JEM-1400 apparatus (LaB$_6$) at 120 kV. The sample was prepared by drop-casting a sonicated dispersion in ethanol on a copper grid. HR-SEM images were collected on a FEI Magellan instrument equipped with an energy-dispersive X-ray (Oxford 80 mm$^2$) spectroscopy attachment.
Electrochemical Testing. We prepared a water based slurry composed of 70 wt % Si/Ag or Si/Au nanopowder, 20 wt % carbon black, and 10 wt % alginic acid sodium salt (Sigma-Aldrich) binder in deionized water; The slurry was cast with a doctor’s blade onto a roughened copper foil (Oxygenfree, SE-Cu58, Schlenk Metallfolien GmbH & Co. KG) or a felt-type copper current collector (Varta Microbattery GmbH) for the operando measurements. The Si based electrodes carried a net silicon loading of 2 mg/cm². The cells were assembled in an Ar-filled glovebox, with O₂ and H₂O contents below 1 ppm. The anodes were assembled in coin cells (2523, NRC, Canada) vs Li metal (Chemetall Foote Corp., USA) or into a home-built cell described in ref27 with glassy paper as separator. Electrolyte solution was a mixture of fluoroethylene carbonate (FEC; Aldrich, < 20 ppm water) and dimethyl carbonate (DMC,Aldrich, <20 ppm water; 1:4 ratio) with 1 mol L⁻¹ LiPF₆ (Aldrich). Coin cells were cycled at 30 °C using BT2000 battery cycler (Arbin Instruments, USA) (three cycles at C/10, therefore 1 C rate: all capacity in 1 h). Cyclic voltammetry was measured with Bio-Logic, multichannel potentiostat at 1 mV/s between 0.8 and 0.01 V vs Li⁺/Li.

Operando Micro-Raman Analysis. Operando cell for electrochemical micro-Raman studies were conducted in a specially designed cell, as shown in Scheme 1.²⁷ The cell allows obtaining Raman spectra of the anode, having a preset potential. The micro-Raman spectrometer (Horiba Jobin-Yvon XploRA with laser wavelength of 532 cm⁻¹ and 1 µm × 1 µm spatial resolution) was used in ambient, as the cell is isolated from environmental effects. Lithium metal served as a counter electrode, and Whatman filter paper, as a separator.

3. RESULTS AND DISCUSSION

Synthesis and Characterization. Noble metal decorated silicon composites (Si/Au, Si/Ag) are synthesized via, previously reported, HF-assisted, galvanic displacement reaction.⁴² Typically, electroless deposition takes place between metal cations and Si nanoparticles in the presence of fluoride solution, to generate various silicon nanostructures.⁴³ Systematic control of the reactants concentration and the reaction time allows the anchoring of metallic particles on Si surface; eventually forming metal decorated silicon nanoparticles (Si/Ag, Si/Au). The transmission electron microscopy images of the product exhibits metallic nanoparticles on the Si surface (Figure 1A,B) and the selected area electron diffraction (SAED) patterns confirm the formation of metallic Au and Ag, with a face centered cubic lattice structure. The silicon is found to be crystalline (Fd₃m, a = 5.4309 Å, JPCDS No. 27-1402).

The X-ray diffraction patterns (XRD) demonstrate the presence of Au (ICCD No. 00-004-0784) and Ag (ICCD No. 01-087-0597) along with Si reflections (ICCD No. 00-027-140) as shown on Figure 2. It is apparent that the harsh, HF based, synthesis conditions do not alter the crystal structure of silicon.

Ex Situ Characterization. Figures 3 and 4 present the scanning electron microscope images of Si/Au and Si/Ag electrodes prior to cycling. An electrode is manufactured by applying a slurry based on these nanoparticles to a copper mesh. Si/Au nanoparticles are uniformly spread on the Cu mesh electrode (Figure 3). Figure 3 reveals the cross-section of the electrode, obtained by cutting the electrode and pasting on the SEM sample holder. The electrode consists of a Cu mesh impregnated with the electroactive slurry; the Cu mesh does not allow for a standard cross-section SEM specimen. The spreading of the slurry into the copper matrix is uniform and similar to the loading of Si/Au on the surface. Energy-dispersive X-ray spectroscopy (EDX) shows that Si nanoparticles are covering the electrode together with Au nanoparticles.
addition, Au nanoparticles are homogeneously spread on the copper mesh (Figure 3C), while Si nanoparticles are mostly concentrated in one region (Figure 3D).

SEM images of Si/Ag electrode are presented in Figure 4. The copper mesh is homogeneously covered with the Si/Ag based slurry (Figure 4A,B). Ag nanoparticles cannot be distinguished on the images, due to their small sizes. However, EDX reveals the uniformly spread Ag nanoparticles on the electrode surface along with Si nanoparticles (Figure 4C,D). The electrochemical activity of Si/Au and Si/Ag was measured in Li-ion coin cells vs Li metal. Cyclic voltammetry measurements of the Si/Au and Si/Ag nanoparticles are displayed in Figure 5A,B respectively.

The measurements are carried out at three scanning rates: the first 10 cycles at 1 mV s⁻¹, the next 10 cycles at 5 mV s⁻¹, and the last 10 cycles at 1 mV s⁻¹. The typical cyclic
voltammograms for silicon undergoing lithiation and delithiation are presented in Figure 5. Two lithiation plateaus at 0.16 and 0.02 V vs Li⁺/Li during discharge and two delithiation plateaus at 0.3 and 0.53 V vs Li⁺/Li during charge can be observed (Figure 5A,B), corresponding to the two main phases of the LiₓSi alloys. The processes are completely reversible since, after the first lithiation, all the phases are amorphous. In addition, Si/Ag particles exhibit slightly slower kinetics at a scan rate of 5 mV s⁻¹ compared to Si/Au, as revealed by the high polarization in the voltammogram waveform (Figure 5A,B).

Capacity measurements and voltage profile of Si are presented in Figure 6. Si particles exhibit an aerial capacity of 2 mAh cm⁻² (Figure 6A). It is clearly seen, that the initial capacity rises to 1 mAh cm⁻² only after first five cycles, and finally grows to 2 mAh cm⁻² after ~14 cycles, indicating the low interconnectivity of Si nanoparticles on the initial electrode state (Figure 6B). This aerial capacity corresponds to a weight capacity of ~1,000 mAh g(Si)⁻¹ (where Si accounts for 70 wt % of the slurry). We chose to report all the results in mAh cm⁻² to clearly assess the high loading of active material (Si) on the electrode. This capacity remains stable for 20 cycles and then starts to fade slightly to 1.7 mAh cm⁻² after almost 60 cycles. The voltage profile of the first cycle of the Si electrode is presented in Figure 6C, indicating typical silicon related lithiation and delithiation voltage plateaus. Panels A and B of Figure 7 present the Si mesh electrode prior to cycling for comparison.
nanoparticles are spread on the copper mesh. The electrode surface seems to be not homogeneous and Si aggregates are clearly seen on the surface. Furthermore, after cycling, Si particles seem to be detached from the electrode and large cracks are present on the copper mesh (Figure 7C). In addition, Si particles’ round shape is destroyed, indicating an irreversible morphology change (Figure 7D).

Operando Characterization. In order to examine the active sites of Si, Si/Ag, and Si/Au nanoparticles, and study their interconnectivity, operando, micro-Raman spectroscopy is applied directly upon the Cu 100 mesh copper collector screen. The chosen electrode zone was divided into small sections of $20 \times 30 \mu m^2$ to carry out the electrode mapping, while the micro-Raman measurement spots were $1 \times 1 \mu m^2$ in size. Previous studies demonstrated that micro-Raman is a powerful tool capable of detecting the quality of the connectivity of the silicon particles to the Cu current collector substrate, as well as connectivity of the particles to each other.

Figure 8 reveals the operando Raman spectra of Si incorporated into 100 mesh copper; each spectrum is collected in charge or discharge at a given potential vs lithium (labeled c and d, respectively, with the potential in volts: c-1.5 stands for 1.5 V in charge). A sharp, typical peak, which corresponds to crystalline Si, is clearly seen at 520 cm$^{-1}$ (Figure 8A,B). The out of plane O=C ring bending mode, which can be attributed to EC, is present at $\sim$714 cm$^{-1}$, and the symmetric vibration of PF$^-_6$ anion is present at $\sim$741 cm$^{-1}$. The broad peak between 885 and 915 cm$^{-1}$ may be attributed to the overlap of Raman peaks of a symmetric ring breathing mode of EC at 900 cm$^{-1}$ and to CH$_3$O stretching of DMC at 916 cm$^{-1}$. The Si peak is decreasing following the discharge potential reduction (Figure 8A). Below the potential of 0.88 V, significant decrease in the Si peak intensity is obvious. In particular, when the discharge potential reaches 0.09 V, the Si peak completely disappears, indicating the formation of an amorphous SiLi$_x$ phase$^{44}$ which is not detectible by Raman and does not recover during the delithiation. Figure 8B presents the spectra of Raman-active sites of Si. Interestingly, some spots of the spectrum have not changed at all during the whole battery cycling, indicating that these areas have not been electroactive during battery cycling.

Noble metals (Ag, Au) enable the SERS effect due to the LSPR phenomenon. To evaluate the electrochemical and Raman activity of the Si/Ag and Si/Au nanoparticles, operando micro-Raman analysis is performed directly on the previously prepared electrodes. The collected spectrum is presented in Figure 8.

A sharp typical peak of Si is present at 520 cm$^{-1}$ for both composites, Si/Au and Si/Ag (Figure 8C,D). Furthermore, in both composites, it is clearly seen that the Si peak is slowly fading until complete disappearance at the voltage of 0.02 V, during lithiation. Moreover, this peak is not restored during the delithiation, indicating the formation of amorphous SiLi$_x$.

Figure 9 displays the mapping of the active material during cycling of the three presented electrodes as follows: Si/Au (A), Si/Ag (B), and pristine Si (C). The dots on each graph represent the locations of measurement zones: an empty dot is electrochemically inactive area, and a solid dot is an electrochemically active one. The “empty spots” did not participate in the cycling process, probably due to either detachment from the Cu current collector or disconnection between neighboring particles. The solid dots on the graphs represent the areas, where the Si Raman peak faded, due to the amorphous nature of the lithiated Si. In fact, these zones indicate the points, which have been electroactive during the cycling process and have lost their crystallinity upon lithium insertion. Compared to pristine Si, Si/Ag and Si/Au display a higher percentage of electroactive sites (Figure 9D).

Comparison of the total number of electroactive sites during cycling of the three presented materials, Si/Ag, Si/Au, and Si, is shown on Figure 9D. It is clearly seen from the graph, that Si/Ag particles exhibit the highest amount of electroactive sites to begin with as well as a significant increase in the filled dots portion upon repeated lithium insertion. On the other hand, Si/Au nanoparticles exhibit less electroactive sites than Si/Ag.
albeit higher electroactive sites than pristine Si electrode. However, it is clearly seen that the composite electrodes present higher activity upon lithium insertion than the Si nanoparticles, indicating higher electrochemical activity of Si with metallic nanoparticles on the surface. The increase in the number of electroactive sites upon cycling, which all three types of electrode share, stemmed from the fact that the lithiation results in active materials swelling in the felt, thus increasing the percentage of Si particles connected to the current collector. Obviously, even pristine Si shows an increase in connectivity based on this volume expansion, but the ratio of electroactive sites starts at the very poor value of 40% for Si compared to almost 60% for Si/Au and all materials thus demonstrate similar improvement upon cycling. A summary of the connectivity in the material is shown on Figure 10.

General Discussion. The HF-assisted galvanic replacement reaction did not alter the Si structure during the synthesis, despite the harsh conditions. The crystal structure of Si is well maintained together with the formation of Au and Ag nanoparticles on its surface (Figure 1 and Figure 2). Si/Au and Si/Ag electrodes show good spreading of the active material on the copper mesh (Figure 3 and Figure 4, respectively). In addition, the cyclic voltammetry measurement results show typical Si associated performance, confirming that these particles are suitable to stand as anode materials in Li-ion battery (Figure 5). Cycling performance of Si electrode shows high areal capacity of 1.7 mAh cm⁻², which remains stable for 60 cycles. However, during the first cycles, the capacity is limited and reaches its peak only after 14 cycles, due to insufficient interconnectivity between the current collector and the active material particles, which significantly improve

Figure 8. Operando Raman measurements collected from electroactive and Raman-active spots of Si based electrodes: electroactive spot (A); Raman-active spot (B) (c for charge and d for discharge with the potential vs Li/Li⁺ (V)); electrochemically active spots of Si/Au (C) and Si/Ag (D); voltage profile of Si with scheme of the Si active material (E); voltage profile of Si/Au with scheme of the Si/Au active material (F).
probably due to the SEI formation (Figure 6). Specific investigation of Si based electrode reveals that the material suffers from irreversible structural changes upon lithium insertion. In fact, after cycling, Si nanoparticles seem to be detached from the copper mesh current collector, and the electrode is completely destroyed (Figure 7). During the operando measurement, the studied materials have presented electrochemical activity, confirming the appropriateness of the current setup. Si nanoparticles, which have been active during the electrochemical process, display a typical, Si related, Raman peak at 520 cm\(^{-1}\) that diminishes as the discharge process prolongs until full disappearance, since the lithiated Si phase is amorphous and cannot be seen by Raman analysis. It is important to mention that when the particles were detached from the current collector, the Raman peak has been present during the whole cycling process (Figure 8). Similarly, Si/Au and Si/Ag nanoparticles also display a Si peak at 520 cm\(^{-1}\), which disappears when the potential reaches 0.02 V (Figure 8). These disconnected zones of Si/Au and Si/Ag as well as Si nanoparticles are unevenly covering the measured areas on the electrode. Si/Ag nanoparticles exhibit the highest amount of active Si particles during lithiation compared to Si and Si/Au nanoparticles, (Figure 9) suggesting an improved connectivity of the active material to the current collector (Figure 10). Moreover, the interconnectivity of the Si nanoparticles also improves in the presence of Ag nanoparticles on their surface.
due to their conductivity properties. In fact, the metal nanoparticles stand as mediators between the active material and the current collector, and among the Si nanoparticle (Figure 9D). Si/Au nanoparticles also exhibit a larger number of electroactive sites compared to pristine Si, implying better inner connectivity of Si nanoparticles and improved attachment to the current collector. It is also important to mention that both metals, Ag and Au, undergo lithiation in voltage ranges similar to Si, which may contribute to the interconnectivity improvement of the nanoparticles. However, since Au lithiation is relatively slow in terms of kinetics, less Si particles are active during cycling. This later point explains the higher connectivity observed with Si/Ag compared to Si/Au: the number of conductive pathways increases with the swelling of both Si and Ag through lithiation of both phases while only Si swelling is observed for Si/Au.

4. CONCLUSION

We reported on the electrochemical performances of anodes composed of silicon decorated with plasmonic metal (Ag and Au), designed for enhancing Raman signal during operando measurements. The micro-Raman mapping of electroactive silicon material zones reveals how the plasmonic metals influence the distribution of silicon active sites during battery cycling. We have shown that the presence of plasmonic metal can enhance the connectivity of the Si particles by almost 50% while considering the same Si anode material with or without metal dots. The ratio of electroactive Si is found to increase from Si to Si/Au and Si/Ag electrodes, and the results are explained in terms of interconnectivity of the particles, the latter displaying the highest volume expansion which explains the connection to the current collector mesh. Consistently, this study demonstrates that the cyclability of Si anode materials for LIBs can be enhanced by adding plasmonic metal nanoparticles to the active material.

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Funding
This work is supported by the Planning & Budgeting Committee of the Council of High Education and the Prime Minister Office of Israel, in the framework of the INREP project. Y.M. thanks the Israeli Ministry of Science, Technology and Space for financial support. Y.E.-E. acknowledges the support and funding of the EU FP7 “Battery and Supercapacitors Characterization and Testing” (BACCARA) Project and Grand Energy Technion Program (GTEP).

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge Dr Luba Burlaka for her kind assistance with TEM.

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