GeO_2/Ge/r-GO hybrid-composite anodes for LIBs: Effect of Ge loading on Performance

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Abstract

Hybrid composites between Germanium (Ge) and carbonaceous materials are promising anode materials for Li-ion batteries (LIBs). The mitigation of reduced cycling ability and rate capability allows for the unhindered benefit of higher capacities in Ge-based anodes. Here, the effect of Ge mass loading on the electrochemical performance of GeO2/Ge/r-GO composites were evaluated as LIBs anode. GeO2/Ge/r-GO composites were synthesized by controlled microwave radiation of ball-milled Ge and sonicated dispersion of graphene oxide (GO). The composite anode at Ge 25% showed greatest cycling retention with 91% after 100 cycles and an average specific capacity of 300 mAh/g (1600 mAh/g Ge). At 75% Ge mass loading the anode suffered with limited cycling retention of 57.5% at the cost of greater specific capacities. The composite at 50% Ge attained advantageous characteristics of both composites with a stable cycling performance of 71.4% after 50 cycles and an average specific capacity of 400 mAh/g (1067 mAh/g Ge. These findings can be used to shape high energy Ge-based anodes and guide future development in energy storage.

Background

- Ge and carbonaceous materials have been extensively studied due to the carbonaceous' component's ability to mitigate the intrinsic problems of to Ge-based anodes
- The mitigation of reduced cycling ability and rate capability allows for the unhindered benefit of higher capacities in Ge-carbonaceous composite anodes
- Ge holds the advantage over Si in certain aspects such as electrical conductivity and lithium diffusivity

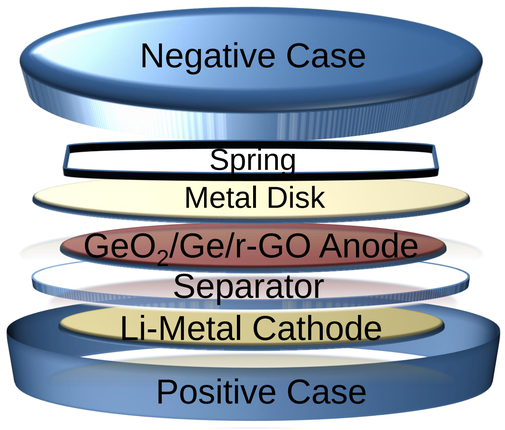
Experimental

- **Material Synthesis**

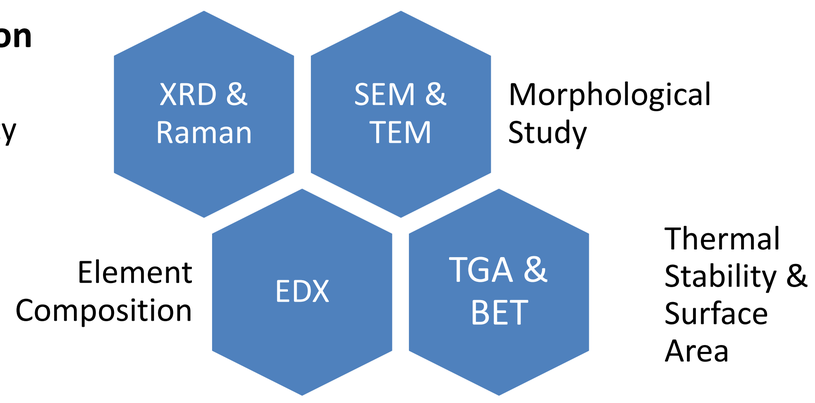
Ball-Milling of Ge-powder → Hummers Method of GO from graphite → Sonication of GO with Ge. → Microwave Reduction of Mixture

- **Cell Fabrication**

Half-cells were made in **CR-2032-coin cells** within a glove box environment (O_2 & H_2O < 0.1 ppm). **Super P, PVDF & NMP** were used with active material-carbon-binder ratio of 0.8 : 0.15 : 0.05 with **LiTFSI electrolyte**



- **Characterization**

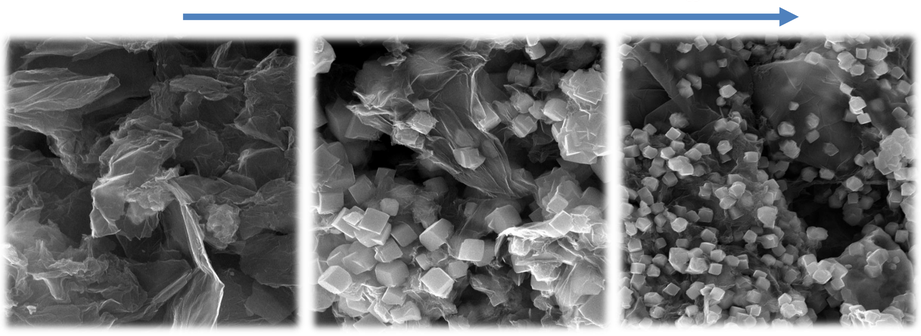


- **Electrochemical Testing and Post-Mortem Characterization**

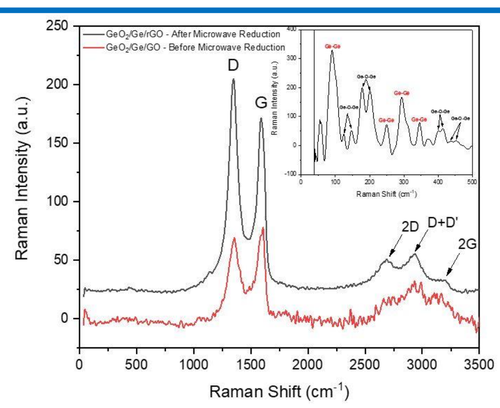
Half-cells were subjected to **cyclic voltammetry** at 0.01 mV/s from 0.05 V to 1.5 V vs. Li^+/Li followed by **GCD** and **rate capability** tests. Cells were further examined under **XPS, XRD, SEM & TEM** at 3 stages; **Electrode-slurry form (ESF), Post-discharge (PD) to 0.05 V *vs.* Li^+/Li and** Post-charge (PC) to 1.2 V *vs.* Li^+/Li.

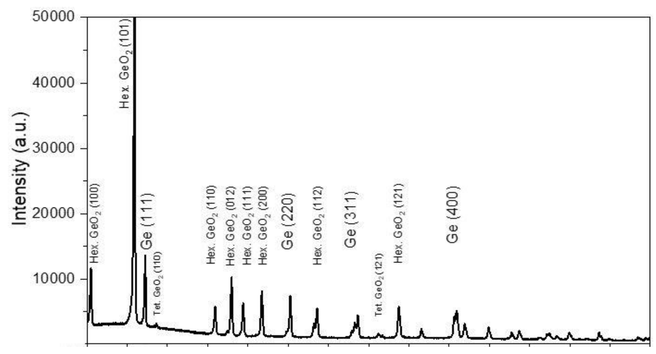
Results and Discussion

Increased Ge Mass Loading

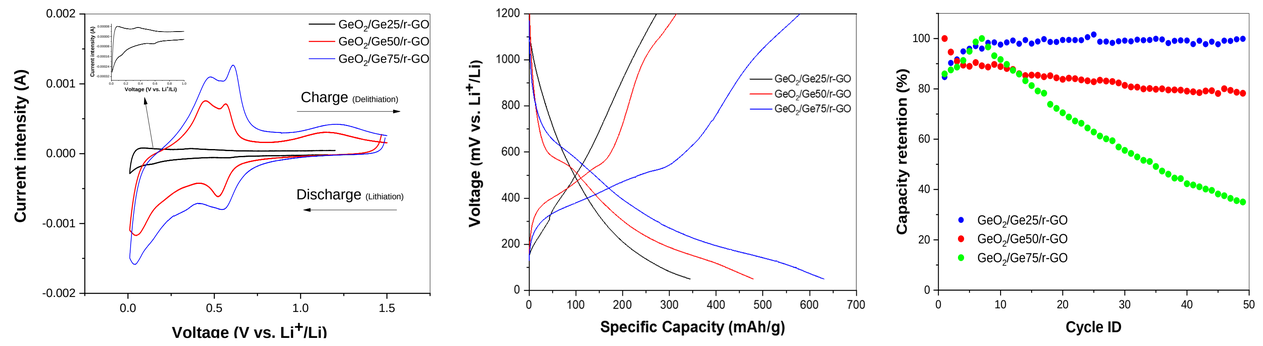


SEM showed the formation of Ge-cubes after ball-milling treatment with average size of 0.8 to 1.2 µm. Increased Ge mass loading lead to greater surface distribution of Ge cubes above the r-GO sheets.

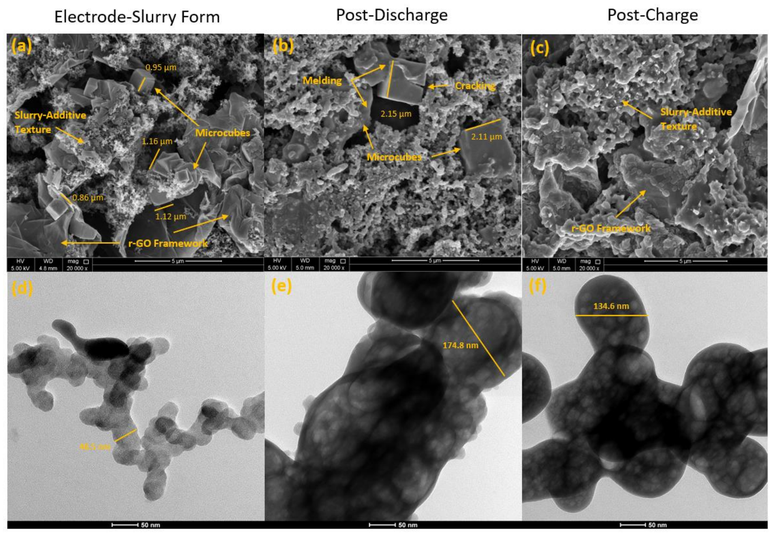




XRD depicts phase-confirmation for Ge and GeO_2 species whilst **Raman** confirmed reduction of GO to r-GO.

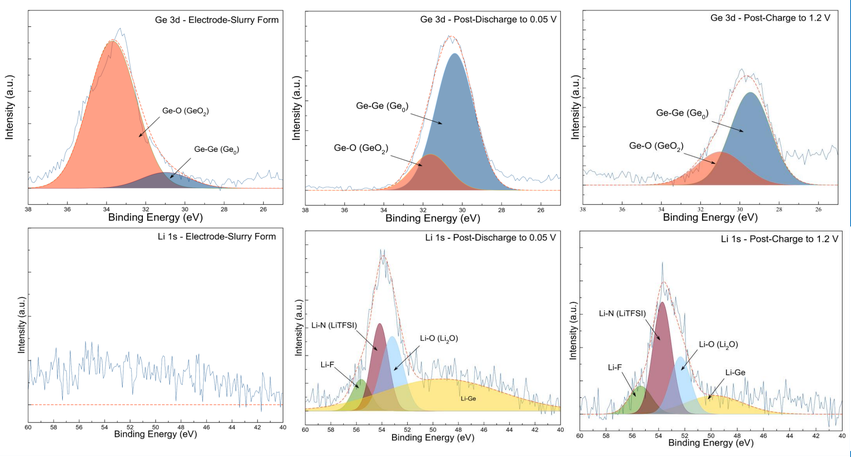


Three wt.% compared in CV and GCD tests. **CV** showed peak development and transitioning with increased wt.%. **GCD tests** show **increased initial charge and discharge** values with **decreased cycling retention** with increased wt.%.



Slurry additives add to texture messiness in Post-Mortem SEM.
SEM shows **increased size of Ge cubes**, as well as **cracking** & **melding**.
TEM likewise shows **increased size** from ESF to Post GCD stages.

Post-Mortem XPS at **Ge 3d and Li 1s spectra**. Key Ge 3d bonds found for **Ge_0 and Ge-O**. Binding energy shifts to lower energy at PC/PD stages hints at formation of **Li_xGe alloys**. Similarly, **Li 1s spectra** shows key bonds and a possible **Li-Ge** bond form at PC/PD stages.



Conclusion

GeO_2/Ge/r-GO composites were synthesized by using a controlled microwave irradiation of ball-milled Ge and sonicated dispersion of GO. Electrochemical characterization of anodes hints at the mechanism changes of lithiation/delithiation with respect to increase Ge loading shifting from Li^+ intercalation/de-intercalation with the r-GO framework to Ge alloy/de-alloying. Ge-based anodes can be a promising alternative to convential anodes for LIBs with higher energy density.

Acknowledgements

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