Synthesizing Highly Crystalline Graphite Powder from Bulk Polyethylene Waste for Lithium-Ion Battery Anodes

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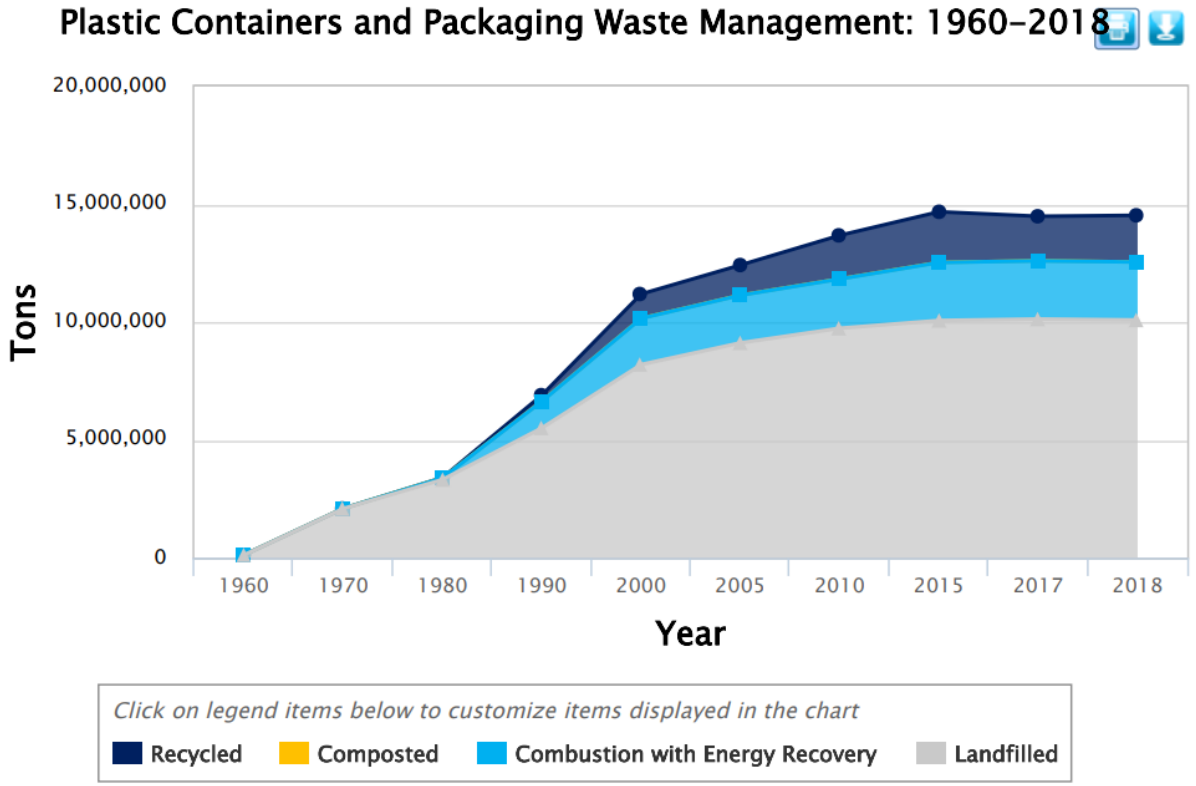
Background



- **8 billion tons of plastic waste has been produced since 1950, but only 6-7% has been recycled.**
- According to the U.S. Environmental Protection Agency, the single use plastics have approximately 12% recycle rate and 16% of plastics are burned with municipal trash each year. The majority — more than 70%, or eleven million tons — is sent to landfills where it can take **hundreds** of years to break down.

Introduction

Conventional Graphitization

- Invented accidentally by Edward Goodrich Acheson in the 1890s:

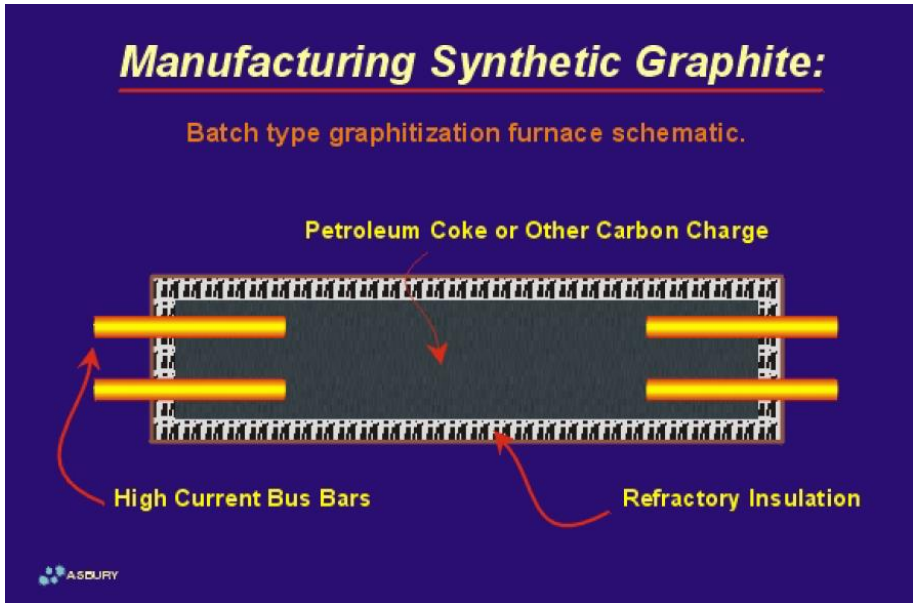
  $3C\ (coke) + SiO_2 \rightarrow SiC + 2CO(g)$ T = ~2000 °C

  $SiC \rightarrow C(graphite) + Si(g)$ T = ~4200 °C

- Current process:

  C (petroleum coke or coal tar) → C (graphite)

T = ~3000 °C, 1–3 weeks



Schematic image of an Acheson type furnace.
(https://asbury.com/media/1225/syntheticgraphiteparti.pdf)

Carbon Feedstock

Catalytic Graphitization Process

T = > 1500 °C, > 3 hours

"Battery-grade graphite"

Introduction

General Requirements for Battery-Grade Graphite

High-Quality Graphite for Battery Application

Low ash (< 0.1%)

- High-purity for max. Li ion loading (theoretical specific capacity of graphite is 372 mAh/g).

Flake graphite (micrometer sizes)

- Highly crystalline flake graphite is essential for high-grade commercial Li-ion grade graphite.

Particle morphology (potato)

- Decreasing Coulombic losses, and a high packing efficiency, increasing volumetric and areal capacity.

Low surface area (< 5 m^2/g)

- Mitigate the solid electrolyte interphase (SEI) formation, mitigate irreversible capacity.

Natural graphite after physical processing

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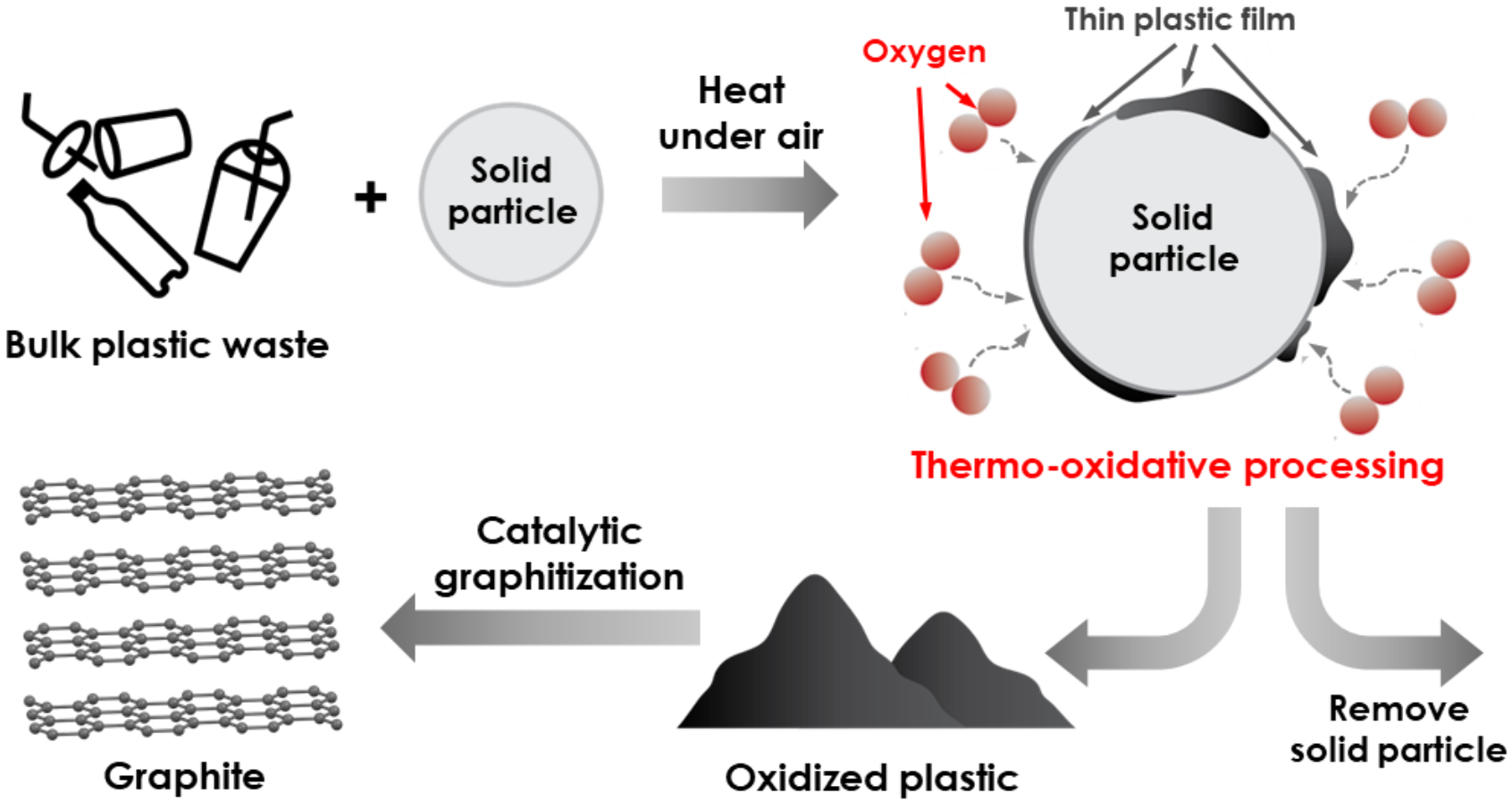
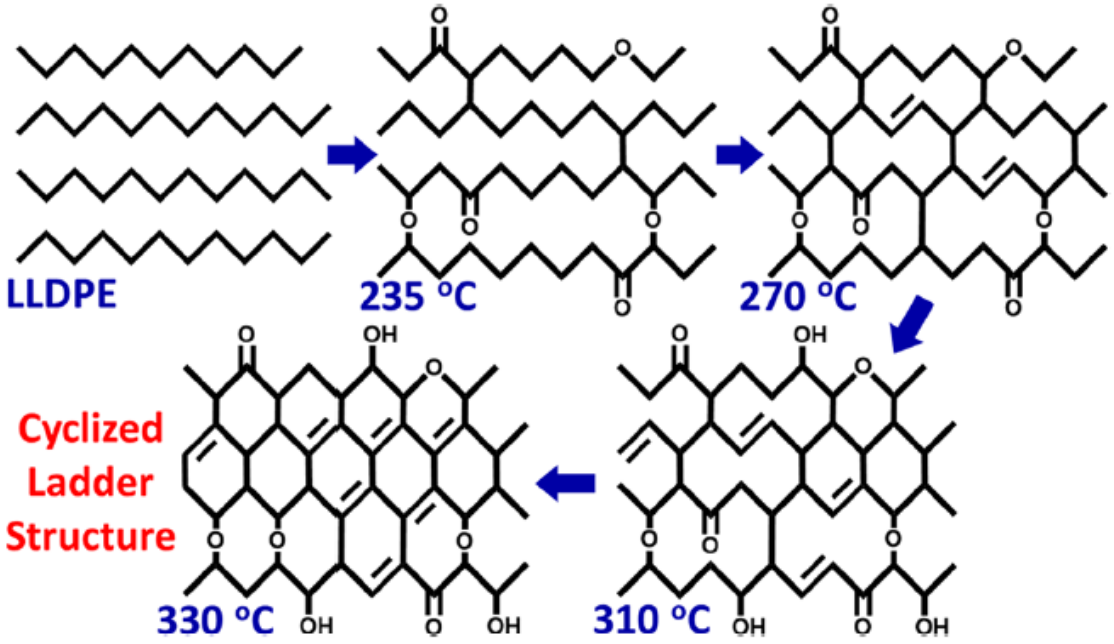
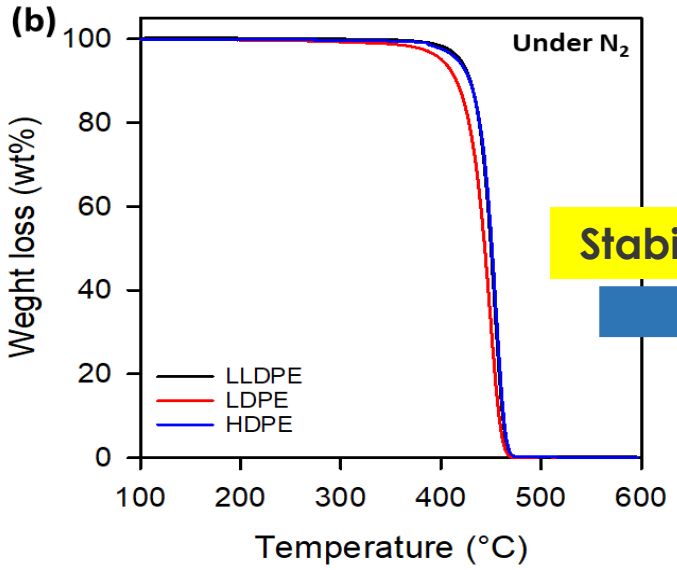
Synthesizing Highly Crystalline Graphite



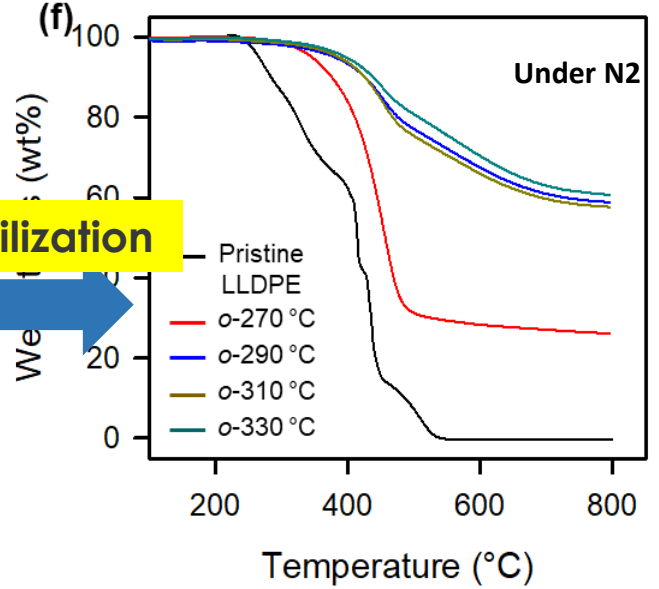
Why Do We Need Stabilization as a Pretreatment?



Mechanism from: Choi et. al., Chem. Mater. 2017, 29, pgs 9518−9527, DOI: 10.1021/acs.chemmater.7b03737.

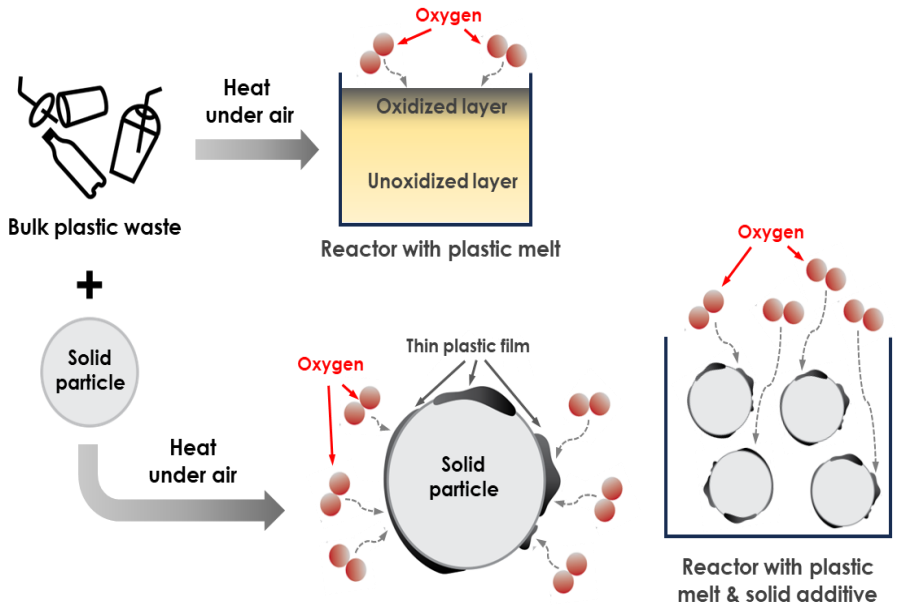


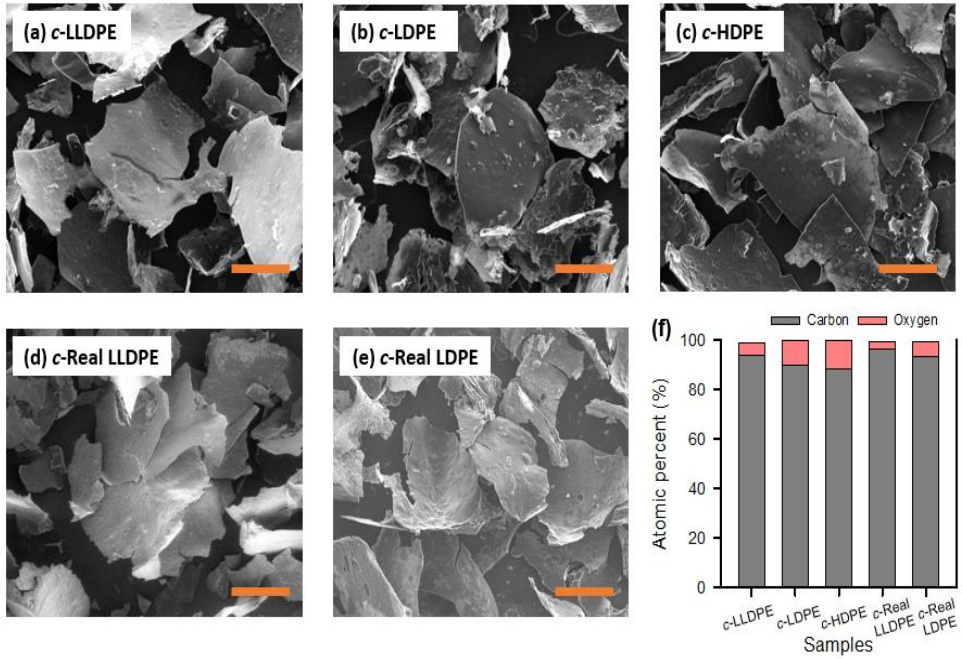
Stabilization



- Stabilization occurs from oxidation and formation of cyclized ladder structures which are more stable at high temperatures than original alkyl chains (left).
- Pre-treating between 290-330 °C stabilizes PE for high temperature processing under N_2 (right two).

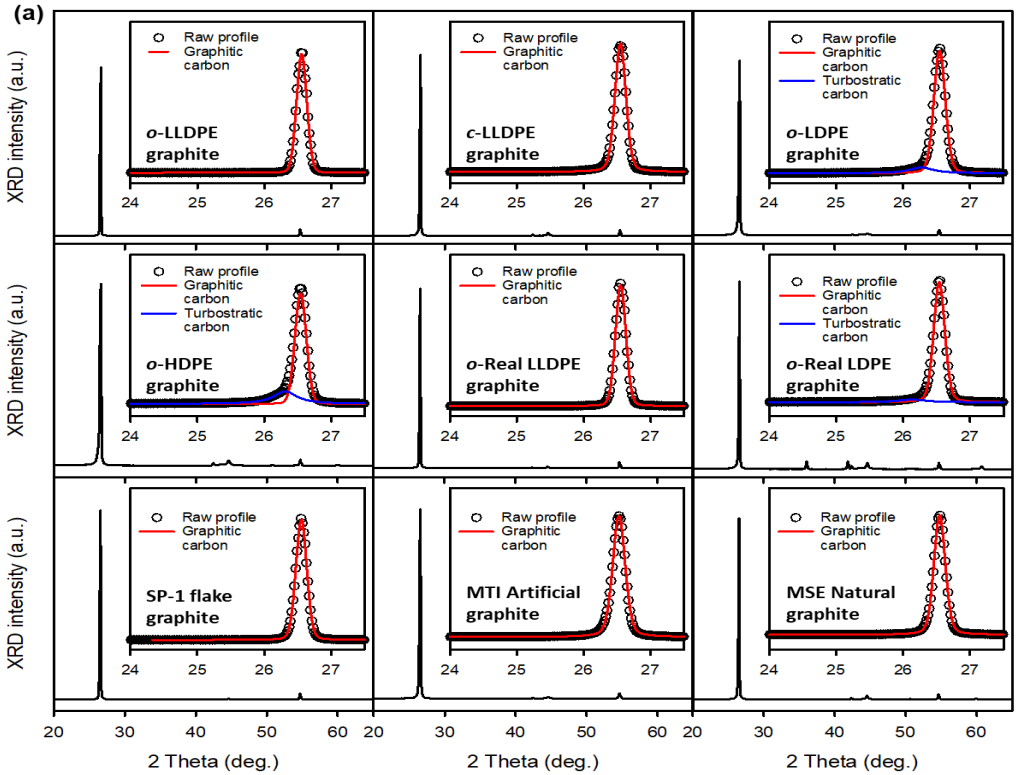
How Do We Do Stabilization in Bulk?



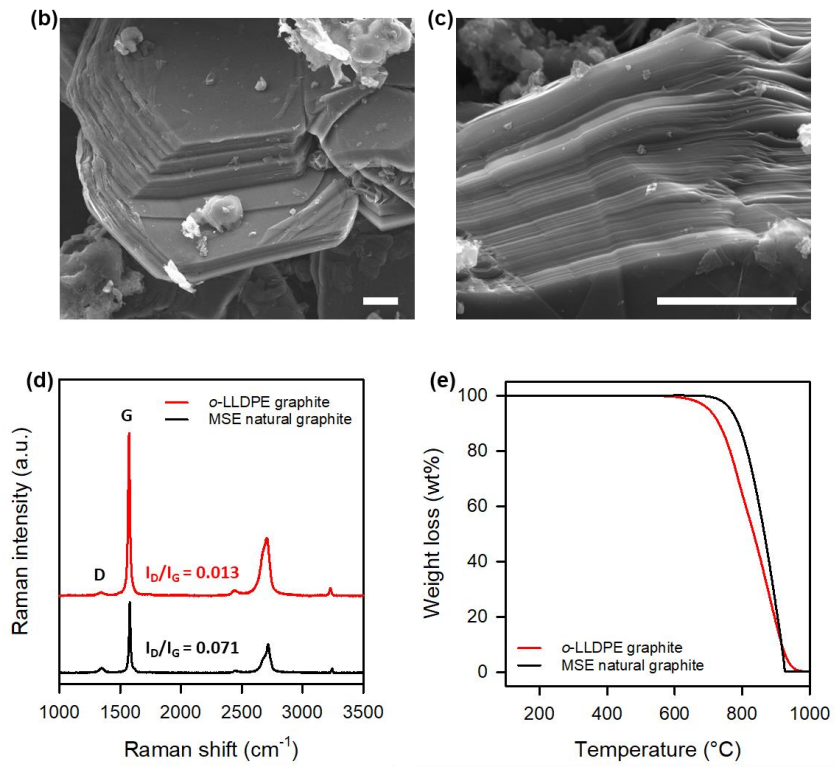


- In bulk vessels, kinetic bottleneck prevents oxygen diffusion into bulk PE melt.
- Adding solid particles (e.g., salt) to PE melt addresses the issue, as it serves as a substrate for thin PE film to form on.
- Film is refreshed constantly with mixing.

Highly Crystalline Graphite Powder from Bulk Polyethylene



Characterization result of o-PE graphite. (a) XRD patterns of the o-PE graphite and three commercial graphite samples. The inset shows the deconvolution results of the (002) peak.



SEM images (b) from above and (c) from the edge of an o-LLDPE graphite crystallite (scale bar is 5 μm), (d) Raman spectra, and (e) TGA curves under air of the o-LLDPE graphite and MSE natural graphite.

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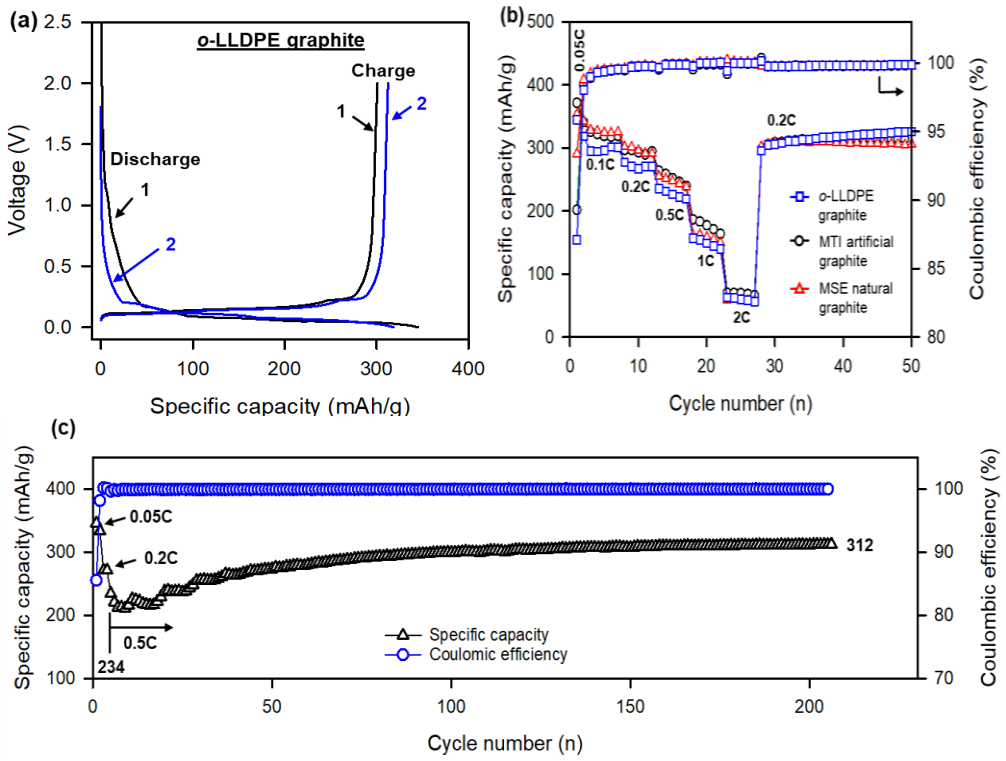
Lithium-ion Battery Test



ICE : Initial Coulombic efficiency
CE : Columbic efficiency

Battery Performance with Graphite Anode

Anode	1st Discharge (mAh/g)	1st Charge (mAh/g)	ICE (%)	2nd Discharge (mAh/g)	2nd Charge (mAh/g)	2nd CE (%)
o-LLDPE Graphite	345	301	87	318	312	98 (99.9)
MSE Natural Graphite	354	330	94	342	338	99 (99.8)

PE-derived graphite has battery performance comparable to natural graphite.

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Summary

- This work demonstrated a simple air processing method for the oxidative stabilization of bulk PEs so these materials can be carbonized and graphitized at higher temperatures.
- Catalytic graphitization of stabilized PE produces a highly ordered graphite powder from bulk PE.
- The PE-derived graphite anode delivers a high reversible specific capacity of 326 mAh/g at 0.2C with a capacity retention of nearly 100% CE after 50 cycles.
- The PE-derived graphite anode shows a reversible rate performance and outstanding long-term cyclic stability, comparable to current-use battery-grade graphite.

Acknowledgments

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