Development of Coal-Based Supercapacitor Materials for Energy Storage

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National Energy Technology Laboratory, U.S. Department of Energy

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Project Team

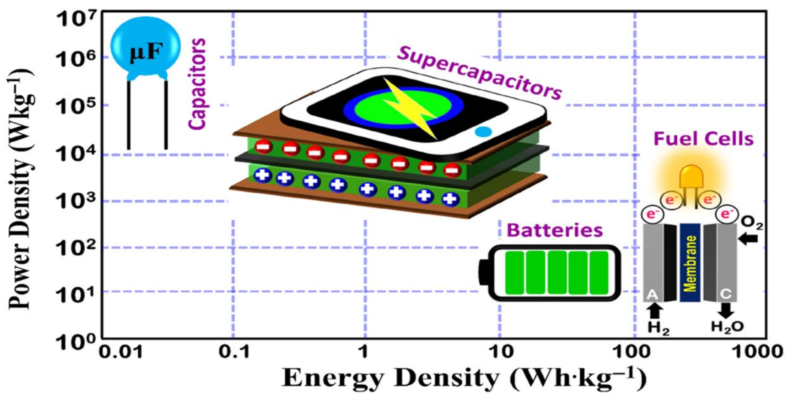
Team Member	Organization	Title	Task Contribution/Role
Heather Dougherty, PhD	DOE/NETL	DOE Project Manager	Project Management
Seyed Dastgheib, PhD	UIUC/ISGS	Principal Research Scientist	Tasks 1-5 (Principal Investigator)
Paul Braun, PhD	UIUC/MRL	Professor and MRL Director	Task 4 (Task leader)
Darshan Sachde, PhD	Trimeric	Senior Process Engineer	Task 5 (Task leader)
Sohan Singh, PhD	UIUC/ISGS	Postdoctoral Research Associate	Tasks 2-3
Rajen Basu, PhD	UIUC/MRL	Research Scientist	Task 4
Fu Wu	UIUC/MRL	Graduate Research Assistant	Task 4
Shuchi Sanandiya	UIUC/ISGS	Research Assistant	Tasks 2-3
Savanna Scheffel	UIUC/ISGS	Undergraduate Research Assistant	Task 2-3

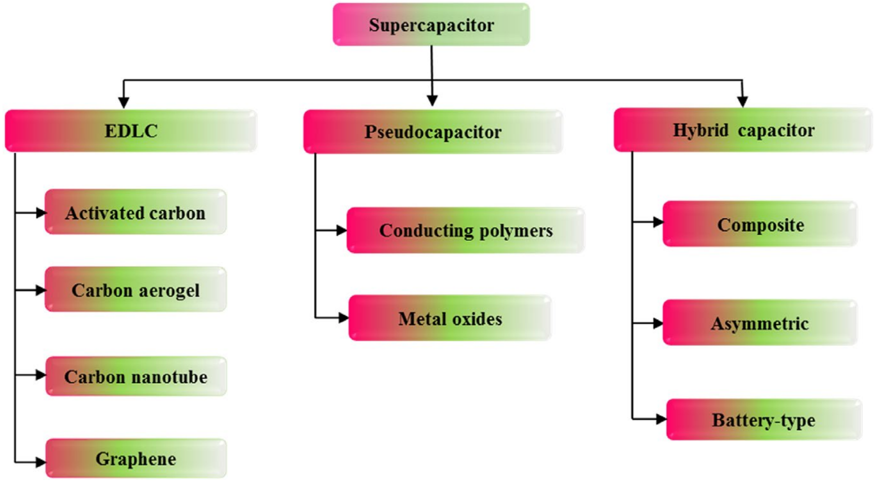
Organizations

DOE/NETL: Department of Energy/National Energy Technology Laboratory
UIUC: University Illinois Urbana-Champaign
ISGS: Illinois State Geological Survey
MRL: Materials Research Laboratory at UIUC

Supercapacitors

- Supercapacitors are energy storage devices that bridge the gap between rechargeable batteries and capacitors.
- The energy storage capacity of SCs is much lower than that of batteries, but SCs can charge and discharge at a much faster rate, even at low temperatures.
- Batteries combined with SCs have currently been proposed as ideal energy storage devices.
- SCs include electric double layer capacitors (EDLC), pseudo capacitors, and hybrid capacitors.

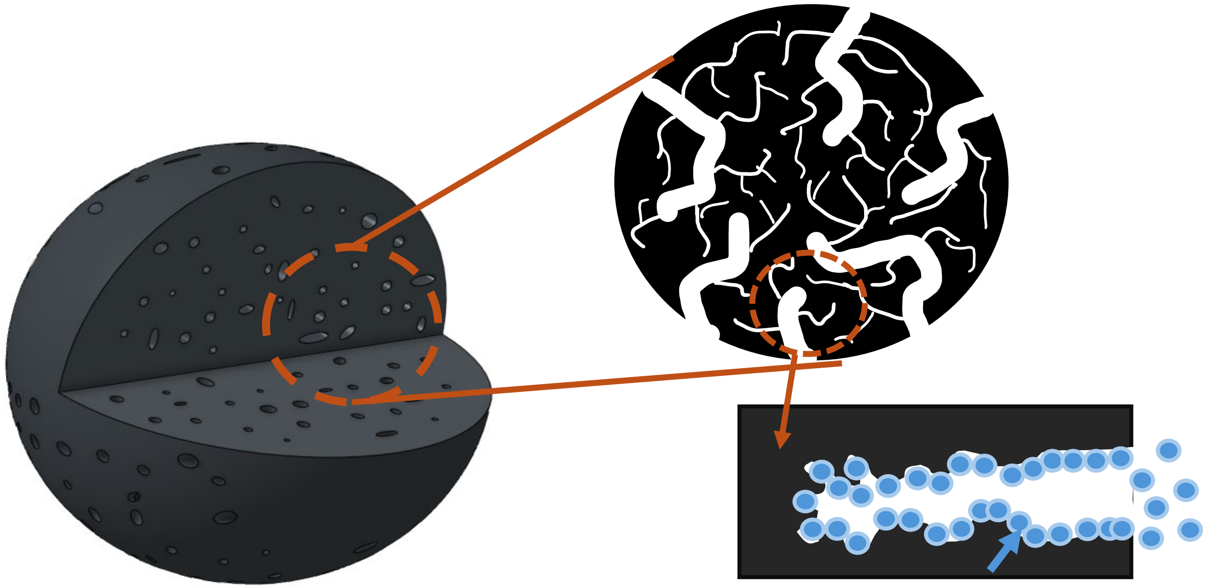




Source: Dutta et al. Energy Storage, Volume: 5, Issue: 1, March 2022, DOI: (10.1002/est2.339)

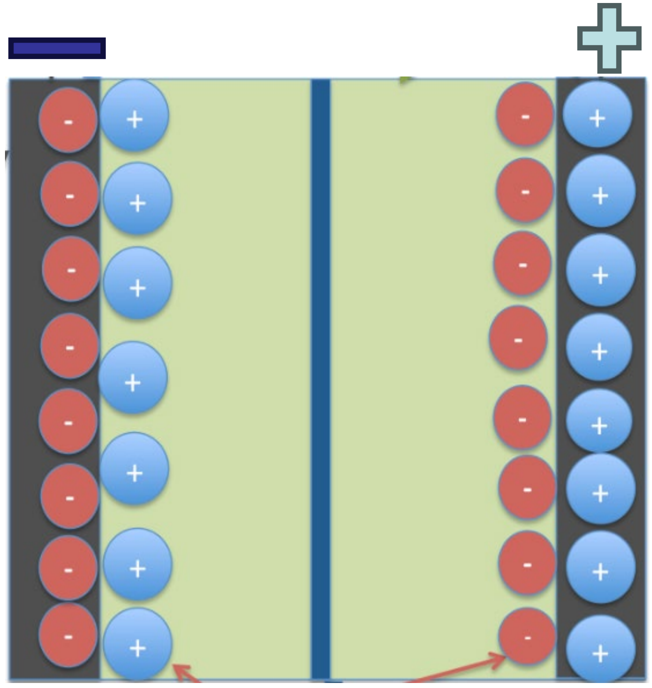
Electrochemical Double Layer Capacitors

- Porous carbon-based materials (i.e., activated carbons (AC)) and carbon nanomaterials are used to fabricate EDLC electrodes.
- Opposite charge (ion) accumulation occurs on the polarized electrode surface with the applied voltage.
- AC provides a high surface area for charge accumulation and energy storage in EDLC supercapacitors. There is no chemical reaction.
- A high surface area, suitable surface chemistry, and other factors contribute to the high performance of carbon-based EDLC supercapacitors.



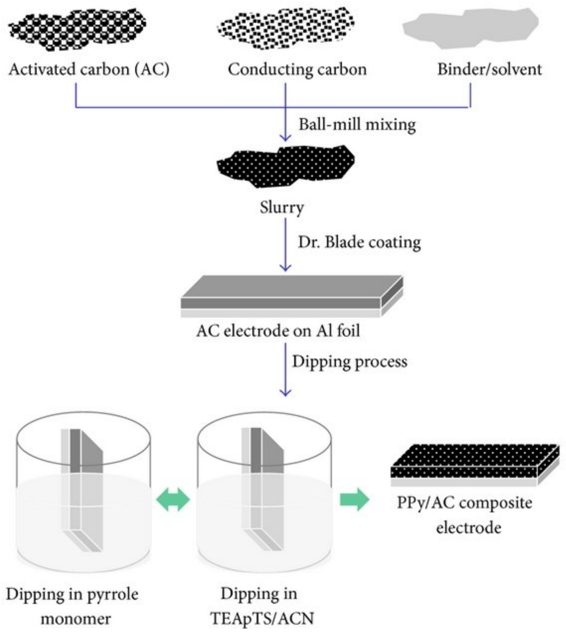
Activated carbon

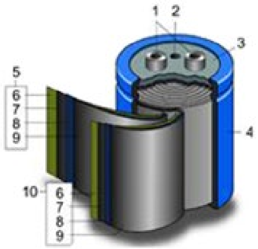
Ions accumulated on the surface in the carbon pores filled with the electrolyte



Fabrication of SC Electrodes from Carbon Materials

- High-grade coconut shell-based ACs are the predominant materials used by SC manufacturers. A conducting carbon additive (e.g., carbon black) is also needed for enhancing the conductivity.
- The AC powder is mixed with a binding material and other additives (e.g., carbon black for enhancing conductivity) and coated as a thin film on a conductive substrate to form the electrode. Electrodes are stacked by placing insulating plastic sheets between them.





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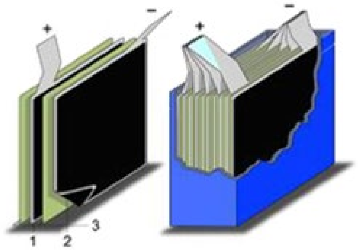

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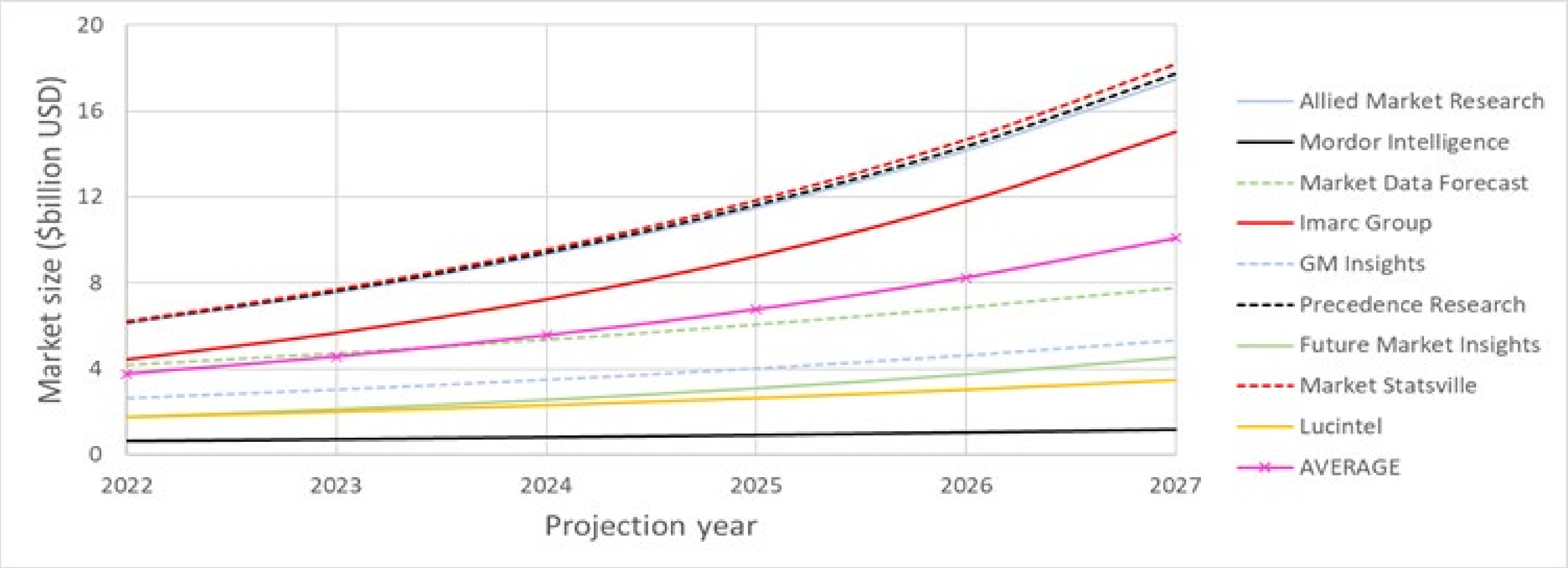
Sources: *Kim K., Journal of Chemistry, 2015, DO - 10.1155/2015/314893.* https://www.digikey.com/en/articles/supercapacitor-options-for-energy-harvesting-systems

Current Price and Market Size of SC-Grade AC

- Reported wholesale price for a SC-grade coconut shell based YP-50F product manufactured by Japanese company Kuraray is ~$30/kg.
- The current market size for SCs is estimated to be between $500 million and $9 billion with a CAGR between 13% and 28% from 2022-2027.



Sources: SC-grade AC price: https://www.alibaba.com/product-detail/Gelon-Wholesale-Activated-Carbon-YP-50F_1600397511059.html. Various market analysis summaries obtained from internet searches used to prepare the figure.

Research Gaps in Coal-to-SC Materials R&D

Current main gaps in coal-to-SC R&D	Proposed approach to advance the SOTA
1. Absence of any comprehensive systematic study on the development of SC materials from different types of coal.	○ Four types of coal (lignite, subbituminous, bituminous, and anthracite) will be systematically processed.
2. Lack of knowledge on the fate of coal impurities (metals, sulfur, halides, etc.) in the production process of SC materials from coal and their impact on the performance of SCs.	○ A deep deashing is included in the process to prepare an ultraclean coal precursor. Fate of impurities in main streams, products, and waste streams will be determined by extensive characterization of the samples.
3. Absence of any work on co-production of both porous (i.e., AC) and graphitic/conductive SC materials (e.g., carbon nanotubes or nanofibers) from coal and their use in fabrication of SC electrodes.	○ Coal-based graphitic or conductive materials will be prepared from coal volatile matter, in addition to the production of porous carbons from coal chars. SC electrodes will be prepared from coal-based materials and tested.

Research Gaps in Coal-to-SC Materials R&D

Current main gaps in coal-to-SC R&D	**Proposed approach to advance the SOTA**
4. Lack of a systematic approach for characterizing coal-based AC materials and assessing their performance for SC applications through <u>comparison with a baseline commercial SC carbon.</u>	○ Both physicochemical characteristics and electrochemical properties of the developed materials and a baseline commercial SC-grade AC will be extensively evaluated and compared side-by-side.
5. Lack of information on the long-term performance of coal-based SC materials for more than 100,000 testing cycles. This information is needed to evaluate potential commercial application of the developed materials.	○ To demonstrate the long-term performance of the developed materials, the best-performing material will be tested up to 100,000 cycles.
6. Lack of a technoeconomic analysis on the development of coal-based SC materials.	○ A technoeconomic evaluation and cost estimation including cost estimation for a plant processing 20 tons of coal per day will be performed.

Project objective, Approach, and Goals

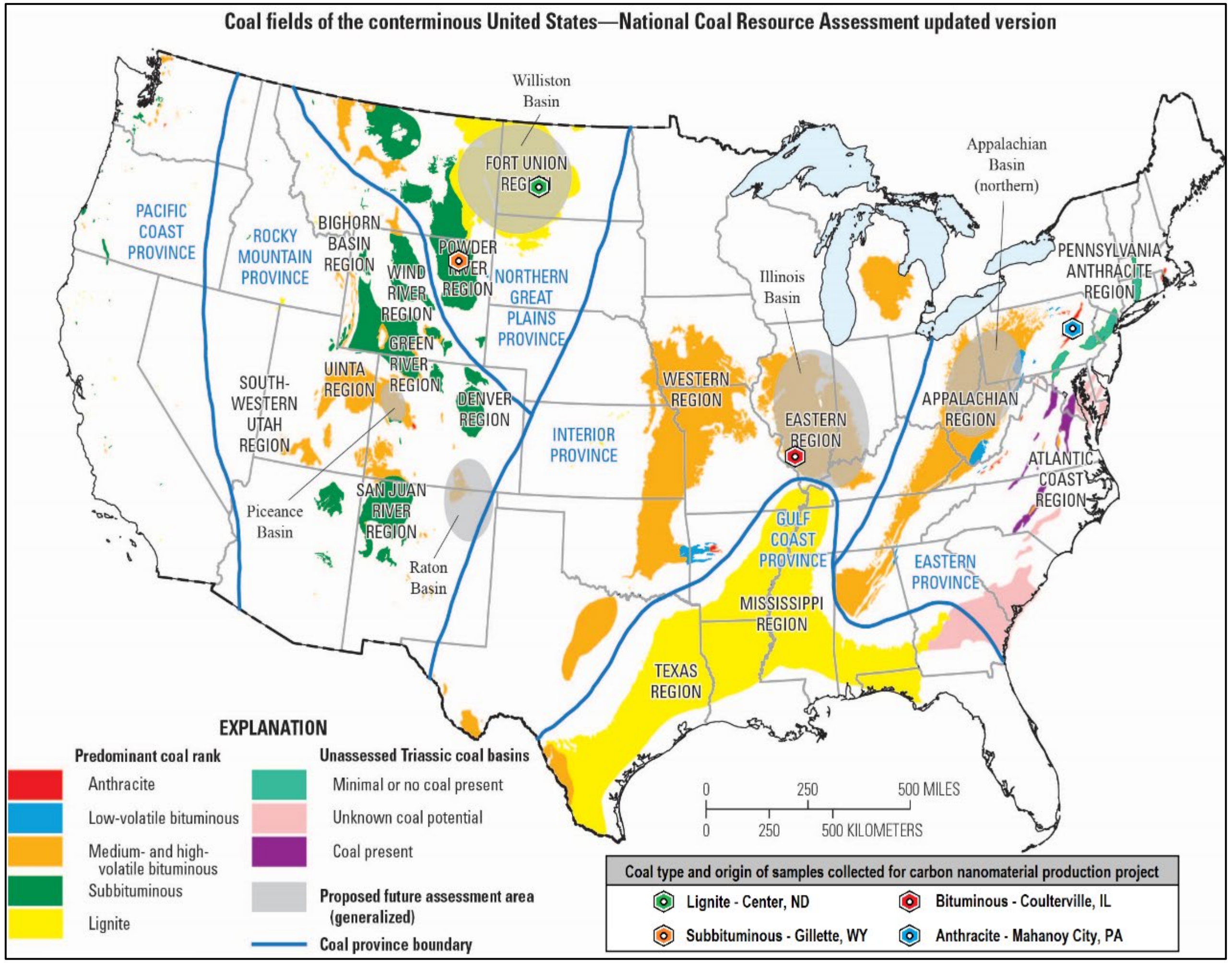
- **Objective** – To develop high-value SC materials from domestic coal in a cost-effective manner

- **Approach**
  - **Coal preparation** – Systematically prepare lignite, subbituminous, bituminous, and anthracite coals by deashing and devolatilization treatments
  - **Development of highly porous functionalized materials** – Prepare materials with surface areas exceeding the surface area of SC-grade activated carbons with suitable surface chemistry for SC application
  - **Development of graphitic or conductive materials** – Prepare materials to be used as the conductivity enhancer additives in fabrication of SC electrodes
  - **Physicochemical characterization** – Perform an extensive physicochemical characterization
  - **Fabrication and testing of SC electrodes** – Fabricate and test SC electrodes from a baseline commercial material and from the developed coal-based materials, perform side-by-side evaluation and comparison
  - **Technoeconomic evaluation** – Perform process simulation, cost estimation, and technology gap assessment

- **Performance and cost goals**
  - Develop cost-effective approaches to produce coal-based materials with a higher capacitance than the capacitance of the baseline state-of-the-art commercial SC carbon material tested under identical conditions. The cost of the coal-based materials should be less than the cost of the commercial material.

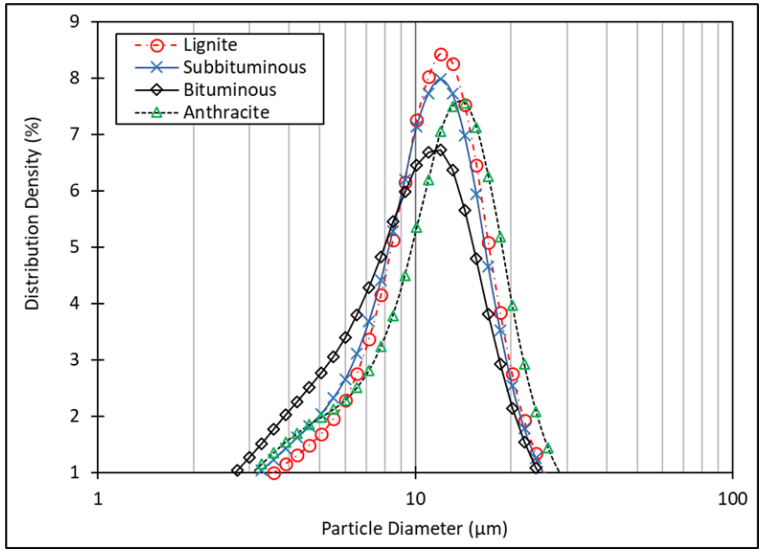
Coal Selection, Preparation, and Characterization

- Four coal samples (lignite, subbituminous, bituminous, and anthracite) are selected, prepared, and characterized



Sources of anthracite, bituminous, subbituminous, and lignite coal samples obtained from different U.S. coal mines are shown on the USGS coal resources map.

	Anthracite	Bituminous	Subbituminous	Lignite
Proximate Analysis (%) - Dry Basis				
Ash	9.5	10.5	6.1	10.3
Volatile	5.0	42.0	43.2	46.3
Fixed Carbon	85.5	47.5	50.7	43.3
Heating Value - Dry Basis				
BTU/lb	13,300	12,740	12,115	11,013
Ultimate Analysis (%) - Dry Basis				
Carbon	84.65	70.50	71.20	68.42
Hydrogen	2.00	5.00	4.90	4.49
Nitrogen	0.70	1.40	1.00	1.04
Sulfur	0.55	3.26	0.29	1.42
Ash	9.50	10.50	6.10	10.34
Oxygen	1.70	9.30	16.60	14.28
Chlorine	NA	0.08	< 0.01	< 0.01



Coal Deashing by Molten NaOH Method

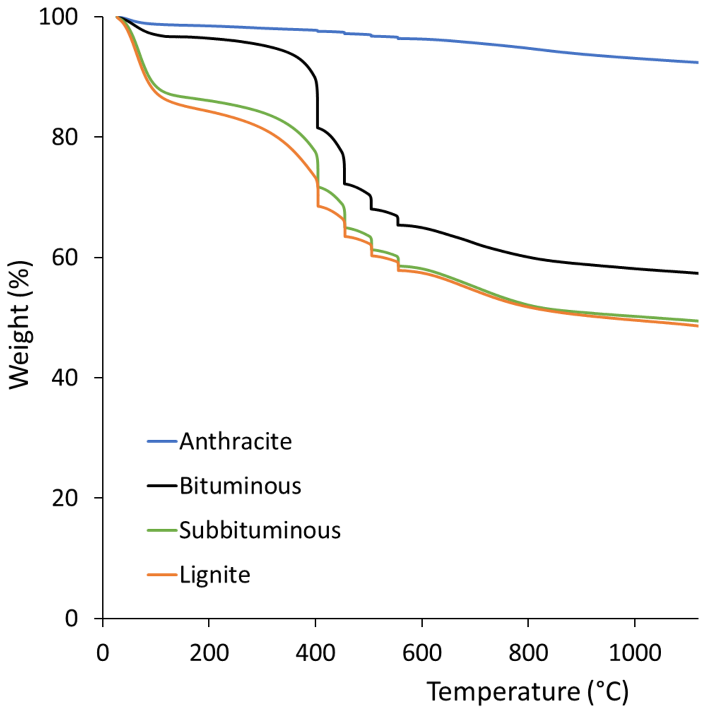
- Coal samples were deashed using the molten alkali method
- Cumulative removal of Ca+Mg+Fe: 95%-100%, Sulfur removal: 65% to 100%, Ash removal: 86-96%
- Deashing approach was highly effective for removal of iron and other transition metals that might have negative impact on the performance of prepared materials for SC application
- For majority of the samples iron is removed to below the detection limit, cumulative concentration of other transition metals in deashed coals is < 100 ppm

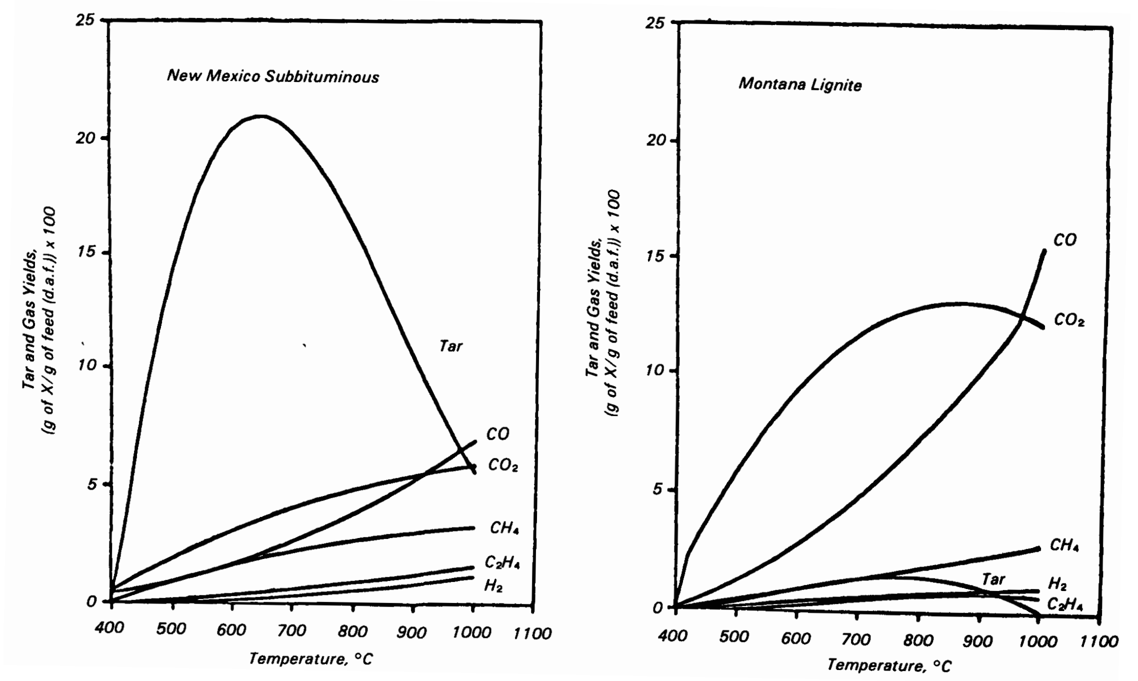
Analyte Symbol	Be	B	Mg	Ca	Mn	Fe	Ni	Cu	Zn
Unit Symbol	ppm	ppm	%	%	ppm	%	ppm	ppm	ppm
Anthracite coal	0.3	2	0.02	0.03	28	0.27	5.6	36.9	11.1
Bituminous coal	0.8	195	0.02	0.38	30	0.28	13.2	11.1	85
Subbituminous coal	0.2	30	0.19	0.97	6	0.1	2.4	10.2	6
Lignite coal	0.5	130	0.32	1.36	56	0.29	4.4	6.7	7.1
Deashed anthracite	0	2	0	0	0	0	2.2	10	0.5
Deashed bituminous	0.2	67	0	0	3	0	7.5	14.1	73
Deashed subbituminous	0	44	0	0.02	0	0	4	17.7	1.3
Deashed lignite	0	43	0	0	3	0.03	7.2	21.8	1.1

	S % (As-received)	S% (Deashed)
Anthracite	0.55	0.195
Bituminous	3.26	0.851
Subbituminous	0.29	< 0.001
Lignite	1.42	< 0.001

Coal Devolatilization

- TGA profiles of as-received coal samples showed a weight loss of ~ 7-45% (dry-basis) when samples heated to 1000 ºC (due to removal of volatiles and decomposition of surface functionalities)
- Several heat and hold sections in the temperature range of 400-600 ºC are included to characterize the release of coal volatiles that occur mainly in this temperature range
- As-received or deashed coal samples were devolatilized by pyrolysis under N_2 at 1000 ºC
- Literature suggests that methane is the dominant hydrocarbon in the gas generated from coal devolatilization at 1000 ºC [Felder and Gilman, 1984]



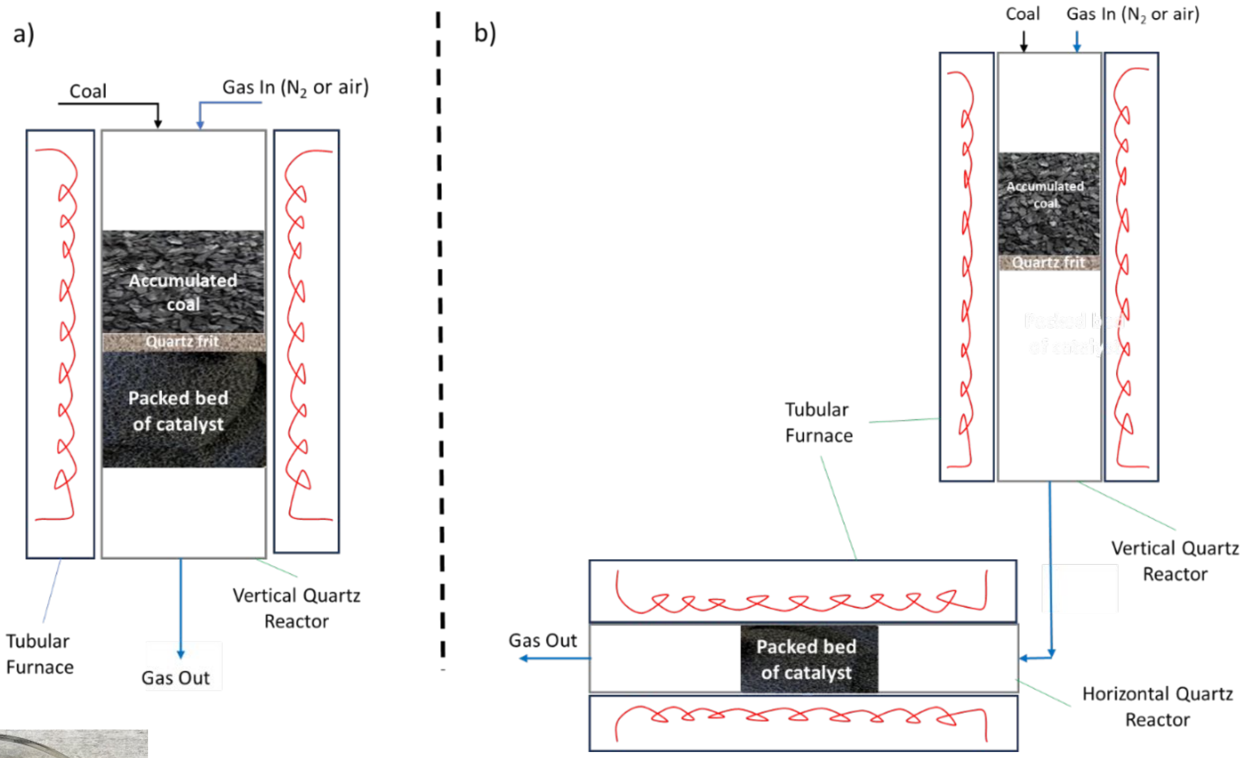


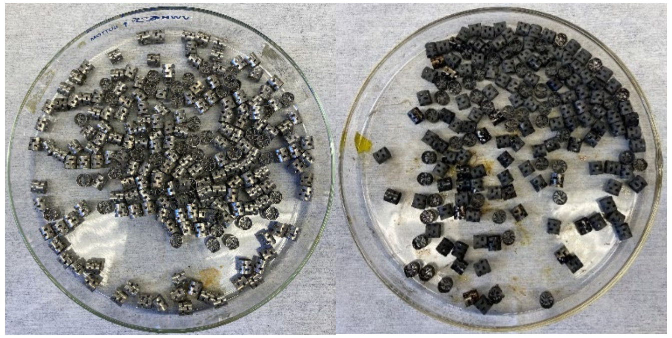
Yield of tar and gases from pyrolysis of two coals (Figure 2 of EPA-600/S7-84-082 Sept. 1984 report by Felder and Gilman).

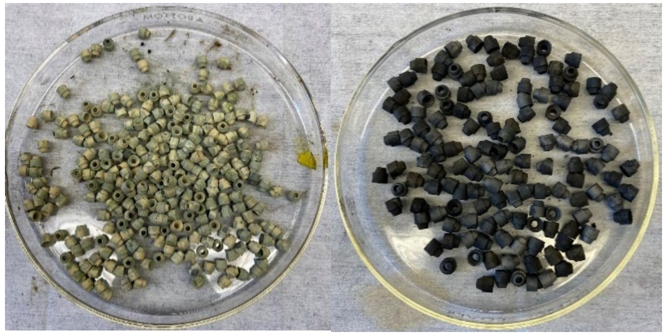
Preparation of Fibrous or Graphitic Carbon from Coal Volatiles

- The catalyst substrate is initially oxidized, then reduced to activate the catalytic sites for carbon deposition and growth.
- After the catalyst preparation stage, coal is added continuously at a constant rate to generate the volatile matter as the hydrocarbon source for carbon deposition on the catalyst substrates that are preheated to a desired temperature.
- Nickel substrates showed the best catalytic performance.
- Baseline experiments were also conducted using methane as the hydrocarbon source.

Continuous generation of coal volatiles and deposition of carbon on a catalyst substrate at the same temperature (a), and at different temperatures (b).

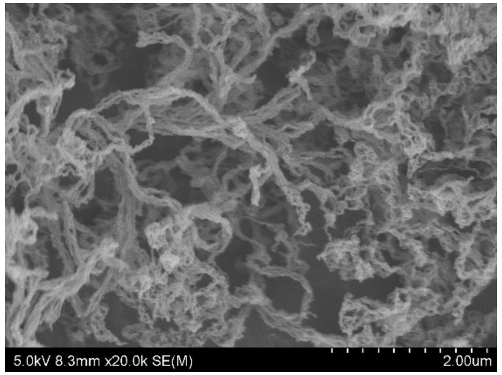


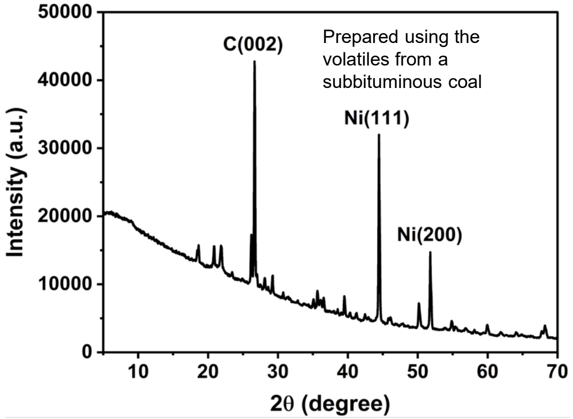


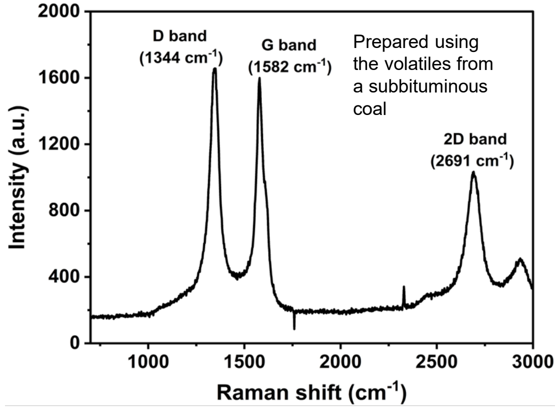


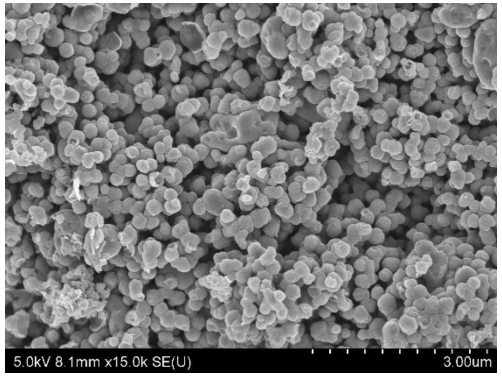
Characterization of Fibrous or Graphitic Carbon Prepared from Coal Volatiles or Methane

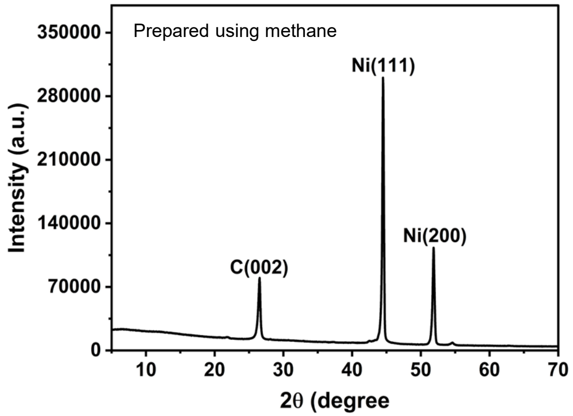
- Samples prepared from coal volatiles were compared with the baseline samples prepared from methane under the same conditions.
- SEM shows fibrous or connected bead type structures that are formed depending on the synthesis conditions.
- Raman spectra of coal-based samples showed D and G bands at the same frequencies as those of the methane-based samples. Compared to methane-based samples, coal-based samples had more defects as indicated by their larger D bands, but they showed similar G bands.
- Majority of coal-based samples and samples prepared from methane pyrolysis also exhibited 2D bands, similar to those observed for multiwall carbon nanotubes or other graphitic materials.
- XRD profiles of coal-based samples showed sharp 26º peaks, similar to those of the methane-based samples.

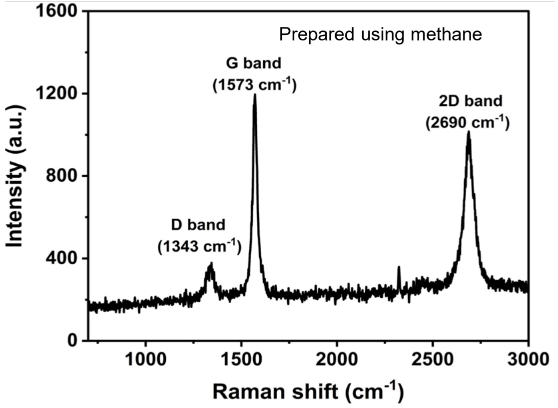












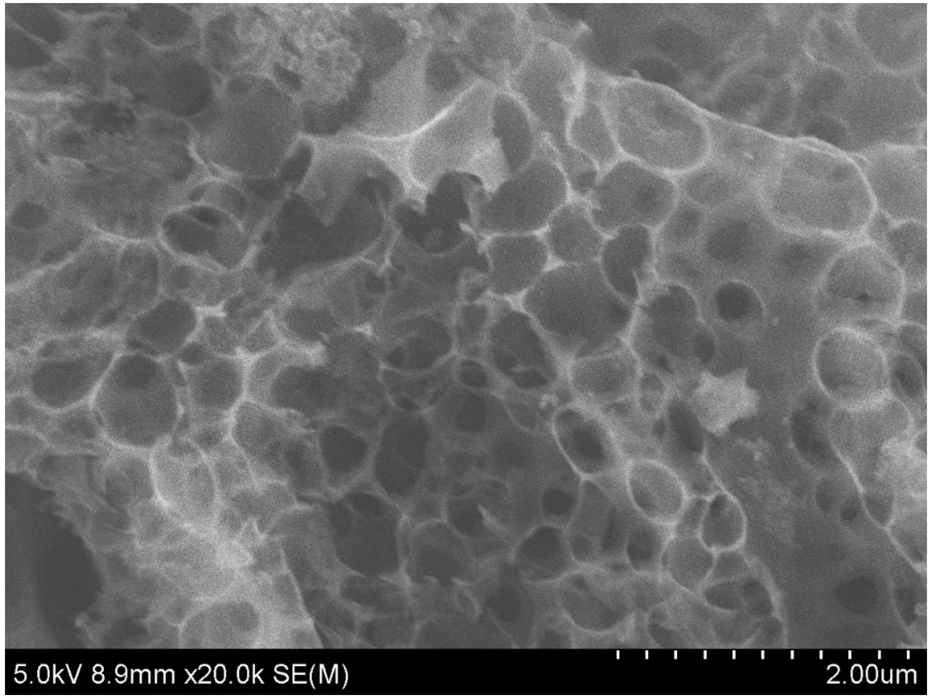
Preparation of Coal-Based Porous Activated Carbons

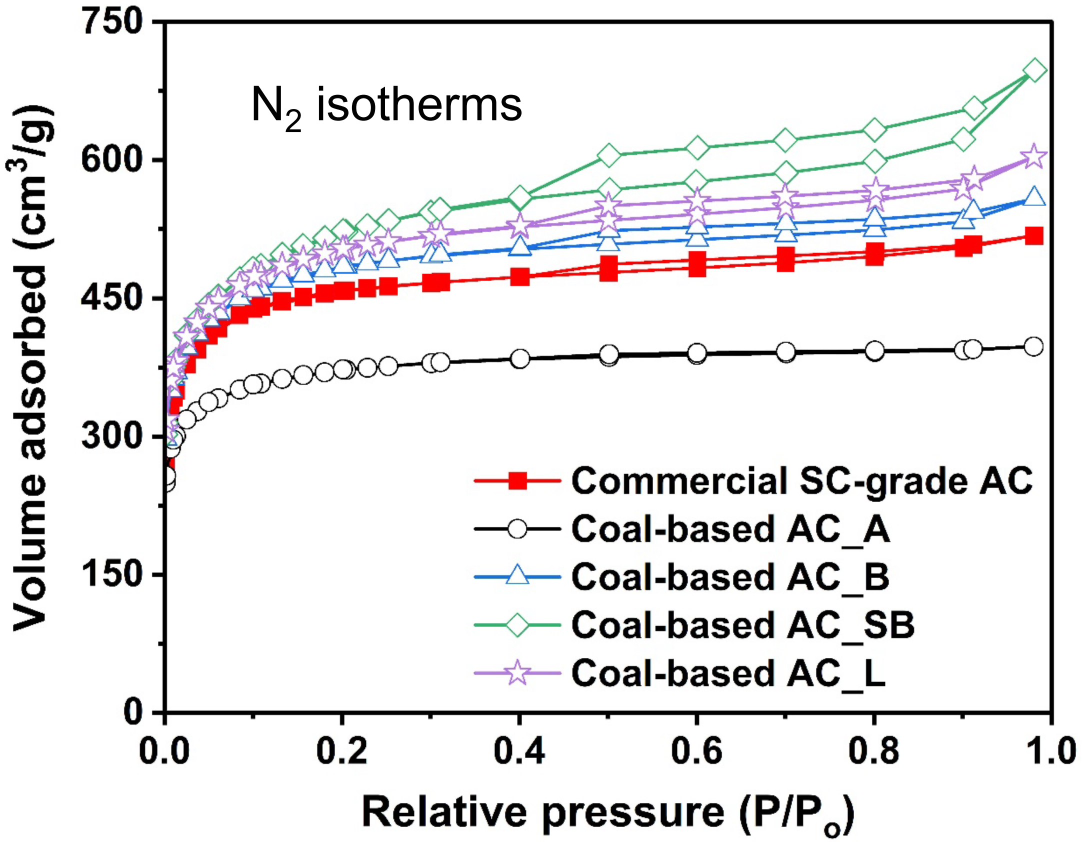
- Work is in progress to prepare highly porous activated carbon from as-received, deashed, and deashed-devolatilized coal chars
- Different activation methods are used
- Porous carbons are functionalized with oxygen or nitrogen functionalities, or impregnated with nanoparticles
- Physicochemical characteristics of the prepared coal-based materials are compared with those of a commercial SC-grade AC

Characterization of Coal-Based Porous Activated Carbons

- Developed materials have a porous honeycomb structure with surface areas of ~1400-1900 m^2/g, exceeding the surface area of the commercial SC-grade activated carbon

	BET surface area (m^2/g)	Total pore volume (cm^3/g)	DR Micropore volume (cm^3/g)	Meso + Macropore volume (cm^3/g)
Commercial SC-grade AC	1717	0.801	0.702	0.099
Coal-based AC_A	1419	0.615	0.561	0.054
Coal-based AC_B	1833	0.863	0.720	0.143
Coal-based AC_SB	1911	1.077	0.754	0.323
Coal-based AC_L	1890	0.933	0.743	0.190





Supercapacitor Electrode Fabrication

Slurry Preparation:
AC (80-90%) + carbon black (2-10%) + additive (5-10%) + solvent (water or organic solvents)

↓

Slurry Mixing

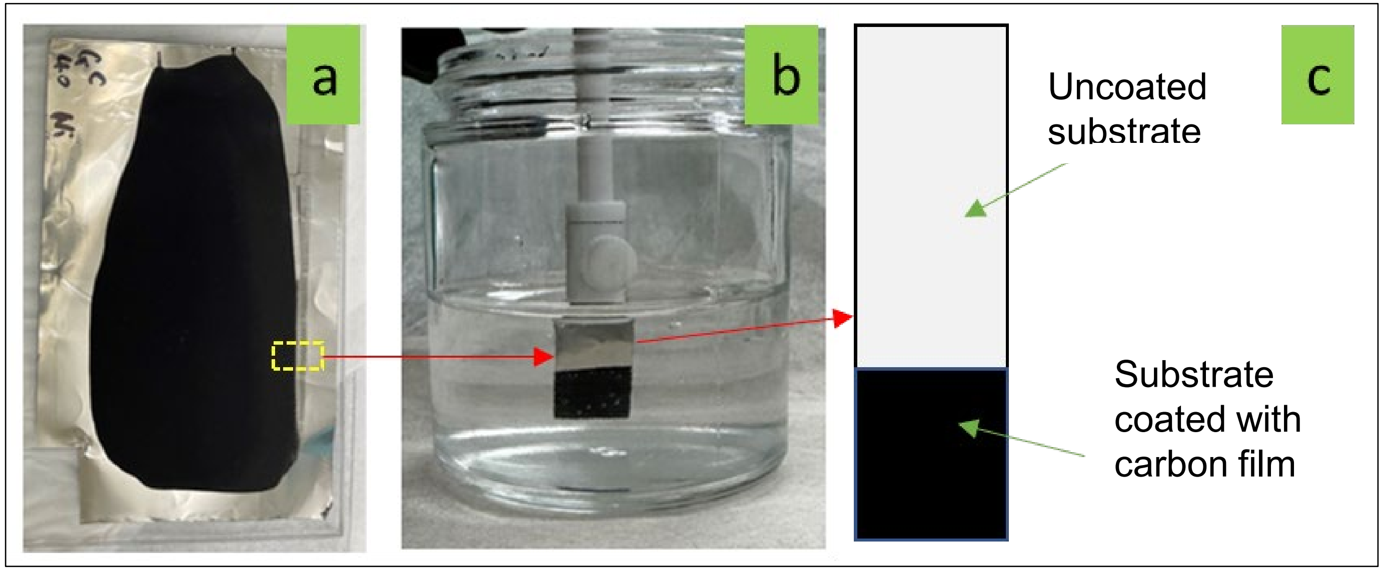
↓

Casting
Spreading a uniform thin film on a nickel foil, drying

↓

Cutting Electrodes

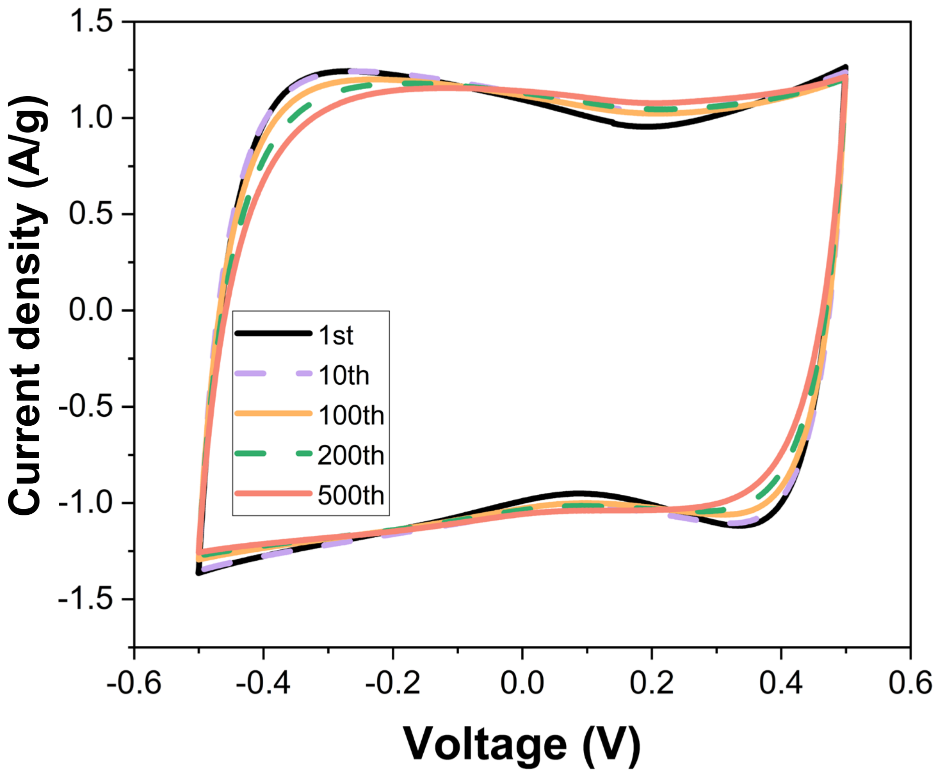
- The optimal conditions of supercapacitor slurry formulation, substrate preparation, film quality including coated film thickness and mass loading were determined.
- Reproducibility within the slurry preparation and coating fabrication processes, and electrochemical testing procedure was demonstrated.

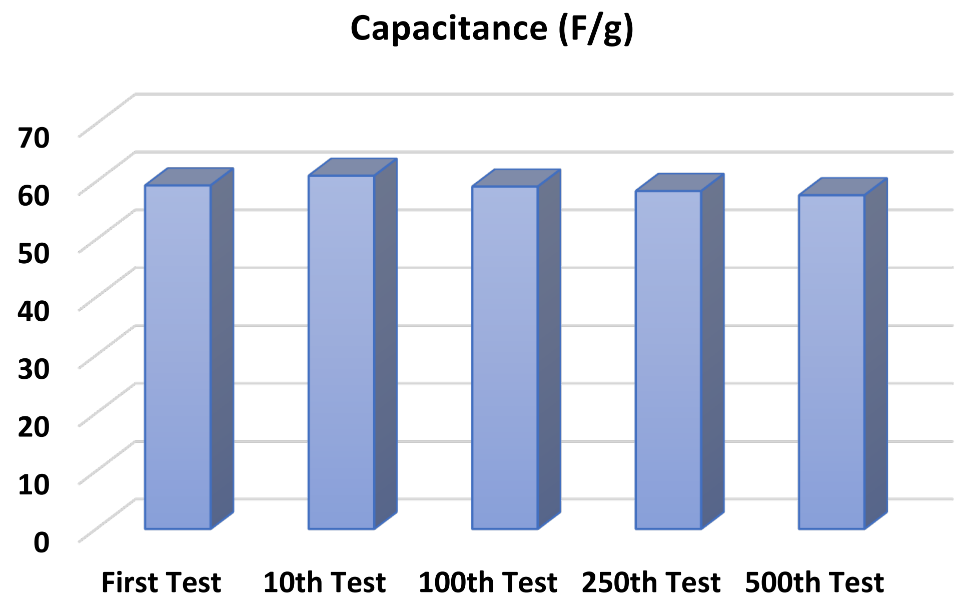


Fabrication of supercapacitor electrodes: a) Slurry-cast carbon film on a Ni substrate, b) Fabricated electrode (cut from the coated substrate) immersed in 1M Na_2SO_4 electrolyte, c) Schematic of a fabricated 1 cm X 3 cm electrode showing coated and uncoated sections.

Baseline Testing of Electrodes Prepared from a Commercial SC-Grade AC

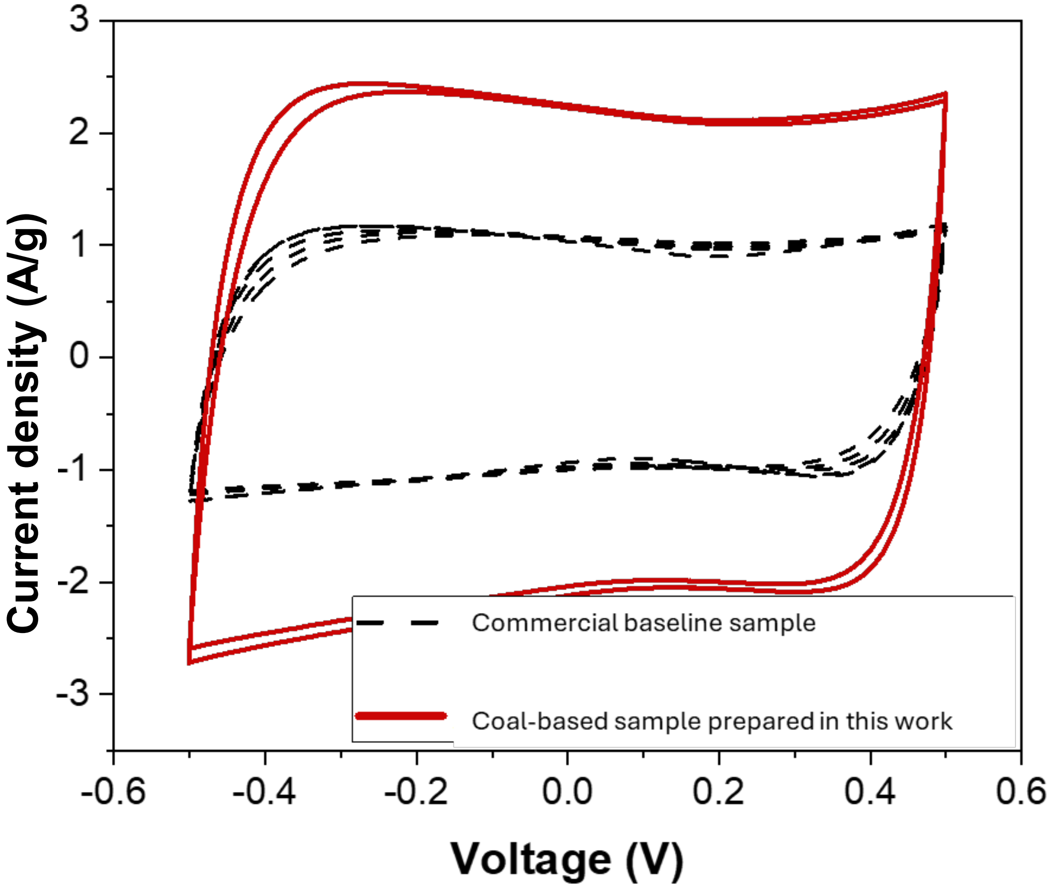
- Cyclic voltammetry tests using a 3-electrode system were conducted to test SC electrodes as the working electrode, platinum coated on titanium mesh as the counter electrode, and Ag/AgCl as the reference electrode.
- Reproducibility of results for a baseline commercial SC-grade AC was demonstrated, by testing multiple electrodes fabricated from different batches and by testing selected electrodes for more than 500 cycles.
- After 500 cycles, the electrode's capacitance was 97.15% of its original capacitance.

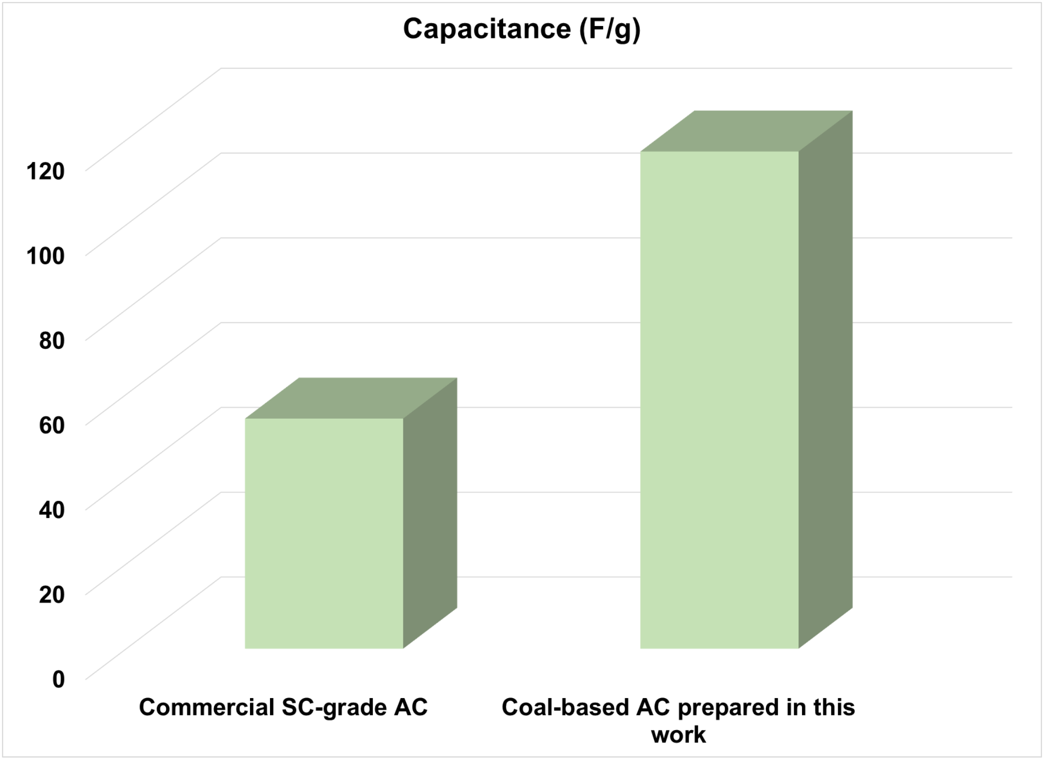




Capacitance Comparison: Commercial Material vs. a Coal-Based Sample

- Commercial SC-grade AC sample: AC mass: 0.0054 g; Film thickness: 70 μm; Capacitance = 54.27 F/g
- Coal-based sample prepared in this work: AC mass: 0.0060 g; Film thickness: 75 μm; Capacitance = 117.27 F/g





Project Next Steps

- Complete the work for preparation and characterization of more than 30 functionalized porous carbon materials
- Prepare additional graphitic or conductive carbon additives
- Fabricate SC electrodes from the developed materials and perform screening tests
- Select the best-performing materials and perform more rigorous testing (using different types of electrodes, longer testing periods, and up to 100,000 cycles test)
- Identify the best performing material based on the energy storage performance
- Perform the technoeconomic analysis and technology gap assessment
- Perform cost estimation for a plant processing 20 tons of coal/day

Summary and Conclusions

- Experimental work performed included coal preparation, removal of coal impurities, coal devolatilization, preparation of porous and fibrous/graphitic SC materials, and an extensive physicochemical characterization.
- Developed coal-based materials have a porous honeycomb structure with surface areas of ~1400-1900 m^2/g, exceeding the surface area of a commercial SC-grade AC.
- SC electrodes were fabricated from a baseline SC-grade AC and from the developed materials. Baseline and lab-prepared electrodes were tested side by side under the same conditions.
- Capacitance of the coal-based electrodes were more than twice the capacitance of the electrodes fabricated from a commercial baseline material.
- Project next steps include preparation and testing of additional SC materials from different types of coal and technoeconomic analysis.

Acknowledgement and Contact Information

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