Engineering pore structure and heteroatom doping of chitin-derived biocarbon by binary molten salt templating for enhanced supercapacitor performance

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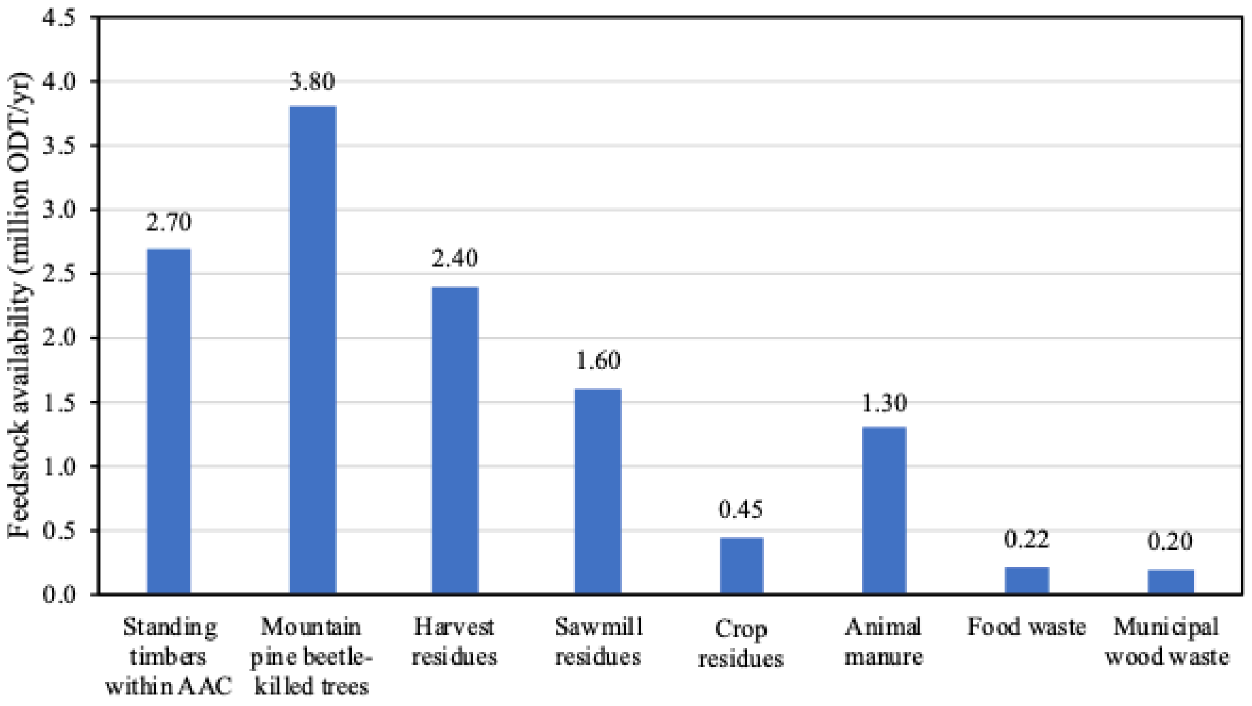
Outline

1. Introduction
2. Experimental approaches
3. Results and discussion
4. Conclusion

Introduction – Biomass wastes



Total amount of biomass wastes in British Columbia, Canada

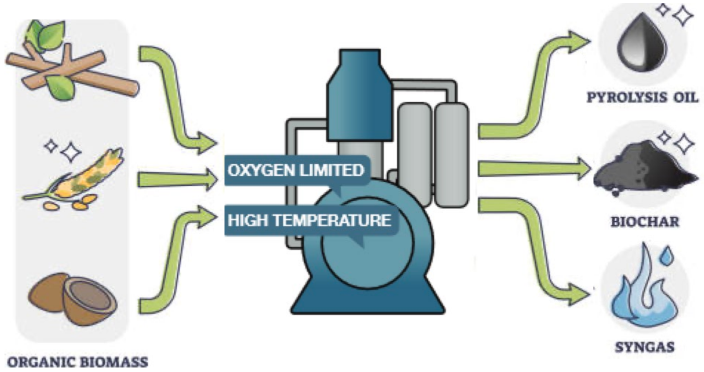
Cellulose pulp

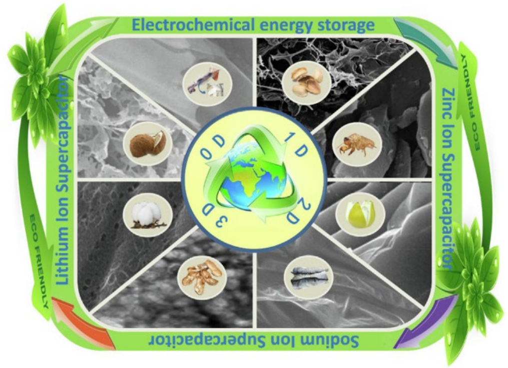
Kraft lignin

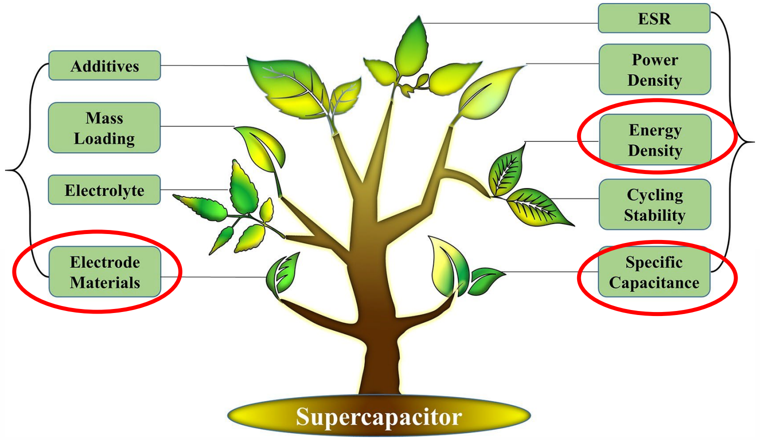
Chitin from crab shell

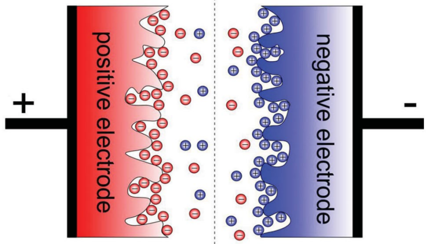
Energy Policy 138 (2020) 111285; https://www.paperpulpingmachine.com/applications/wood-pulp-making/; https://sigmafertilizers.com/; https://www.zeninternational.net/.

Introduction – Biocarbon for energy storage (supercapacitors)







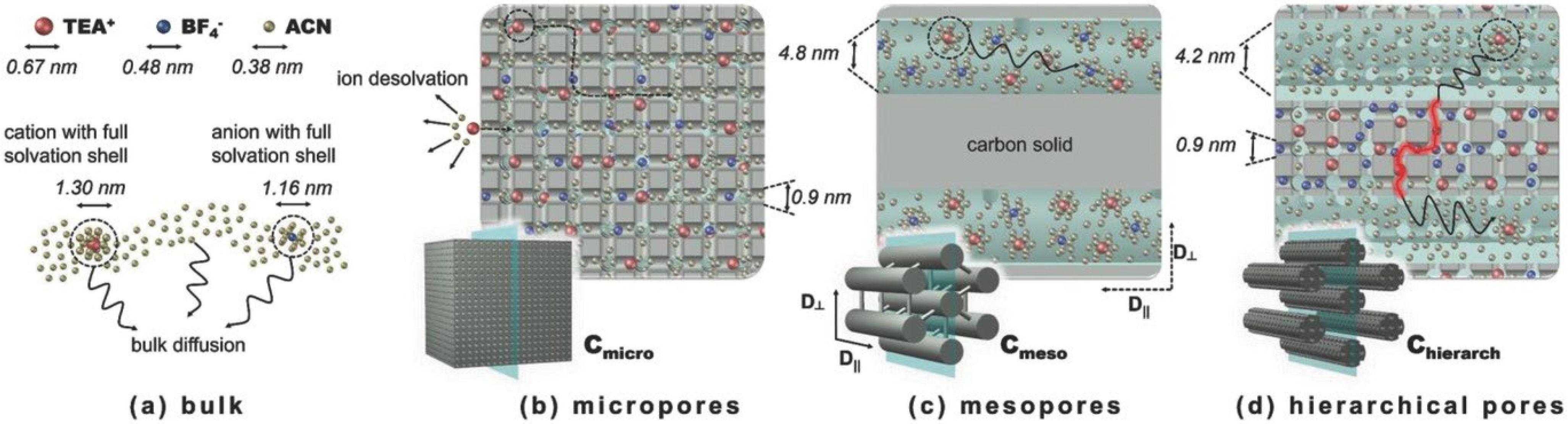


$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

C: Capacitance
A: Surface area of the electrode

https://www.thecarbonic.com/post/better-biochar-is-a-climate-change-antidote; Chemical Engineering Journal, (2020), 125418, 397; Carbon 155 (2019) 706-726; Adv.Mater.2014, 26, 2219–2251.

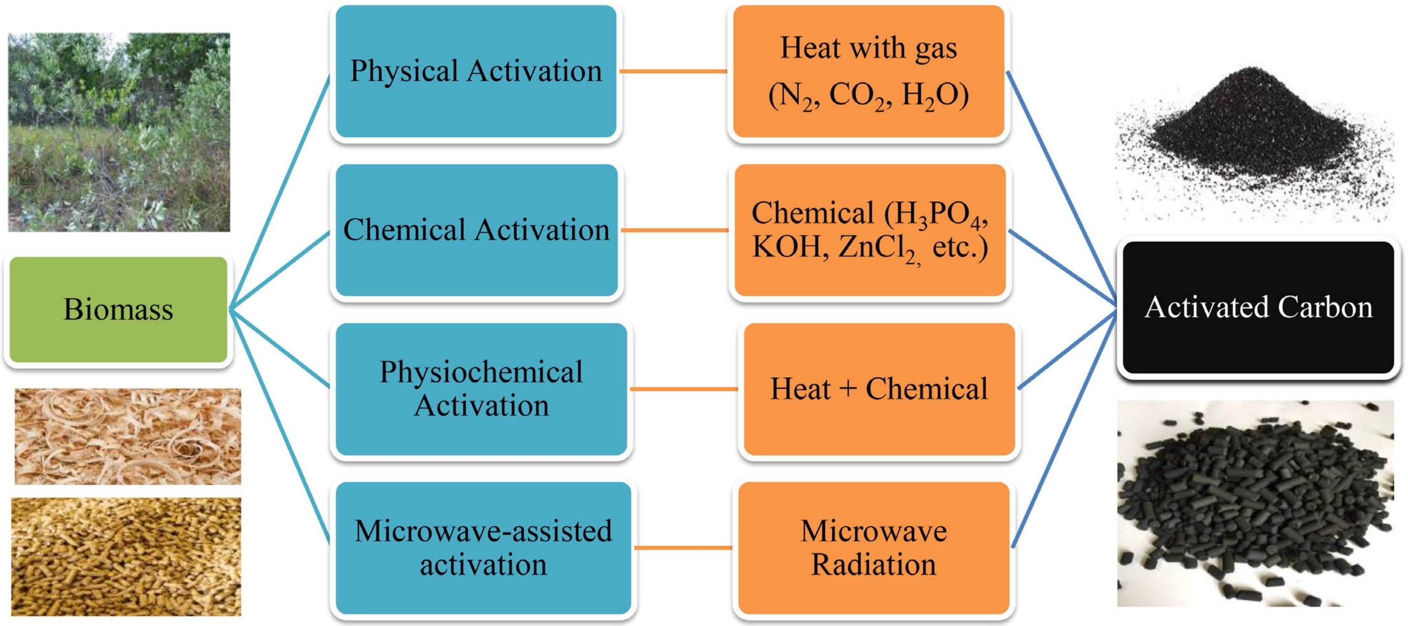
Introduction – Hierarchical porous structure



- Micropores: ion adsorption (optimal size ~0.7-0.8 nm)
- Mesopores: ion diffusion (reduce internal resistance)
- Macropores: ion reservoirs and surface functionalities

Adv. Energy Mater.2018, 8, 1800892.

Introduction – Traditional activation strategy

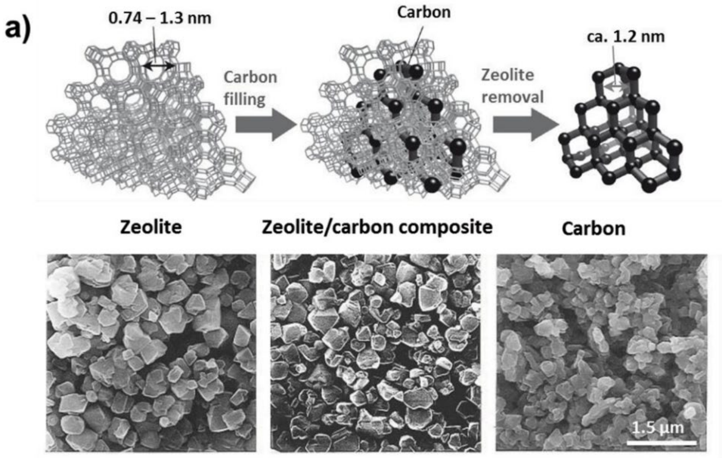


- Bottleneck/slit microporous structure – limited mass transport
- Low carbon yield and non-recyclable
- Rarely allow control over pore morphology and size

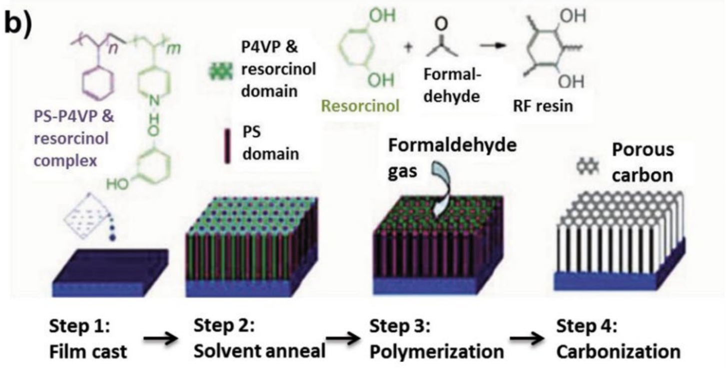
Arab Journal of Basic and Applied Sciences 27(1):208-238.

Introduction – Traditional templating strategy

Hard templating
- Complicated steps and high cost
- Environmental issues
- Low carbon yields



Soft templating
- Intricate and rigorous design on template synthesis
- High cost and non-recoverable



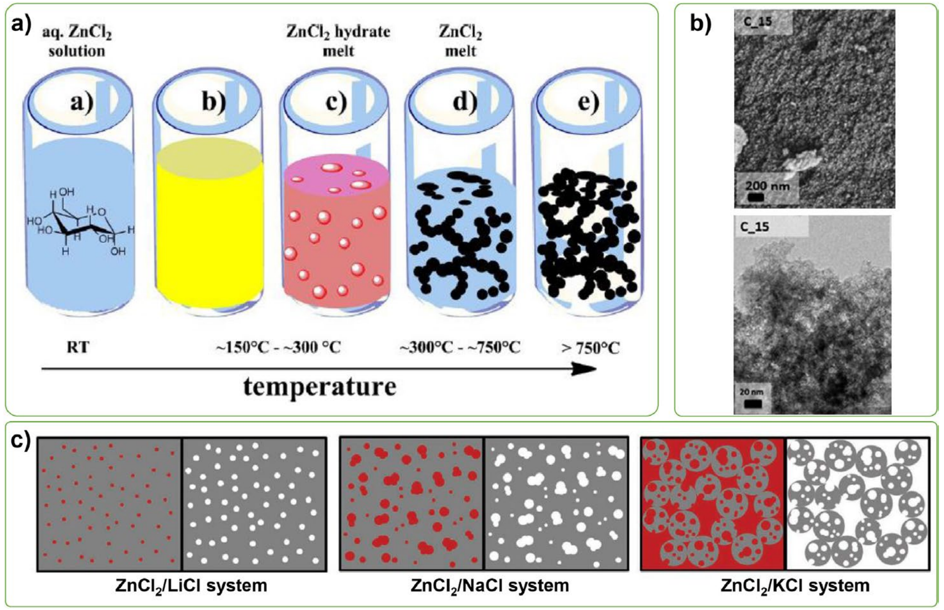
Adv.Mater.2014, 26, 2219–2251.

Introduction – Molten salt templating

Salts	T_m (°C)	Eutectic salt mixtures	Molar ratio	T_m (°C)
$CaCl_2.6H_2O$	30	$ZnCl_2/KCl$	0.54 / 0.46	230
$FeCl3.6H_2O$	37	$ZnCl_2/NaCl$	0.68 / 0.32	260
$MgCl_2.6H_2O$	117	$ZnCl_2/LiCl$	0.78 / 0.22	275
$CaCl_2.2H_2O$	175	KCl/LiCl	0.41 / 0.59	353
$ZnCl_2$	290	$MgCl_2/KCl$	0.30 / 0.70	423
$FeCl_3$	308	$MgCl_2/NaCl$	0.43 / 0.57	459
LiCl	605	$CaCl_2/NaCl$	0.52 / 0.48	504
$MgCl_2$	714	$CaCl_2/KCl$	0.25 / 0.75	600
KCl	770	KCl/NaCl	0.49 /0.51	657
$CaCl_2$	772			
NaCl	801			

Unique advantages

- Hierarchical porosity manipulation
- High carbon yield (20-60 wt.%)
- Good recyclability
- Economic and potential scale-up



a) Sol-gel synthesis of glucose-derived aerogel-like carbon under melted $ZnCl_2$
b) SEM and HRTEM of glucose-$ZnCl_2$ mixture derived carbon
c) Varied pore formation mechanisms for carbons templated with different $ZnCl_2$-based eutectic chlorides

Adv.Mater.2014, 26, 2219–2251.

Experimental approaches

Objectives:

1. Produce biocarbon particles with tunable hierarchical porous structure via molten salt templating.
2. Target high specific capacitance and good rate capability at high current density (50 A/g).

Methods:

- Feedstock: Chitin from shrimp shell
- Experimental setup: Conventional tube furnace under N_2 atmosphere
- Temperature: 800 °C
- Binary molten salt system: $ZnCl_2$-$CaCl_2$ (Zn-Ca)
- Parameter: Ratio of salt to chitin (e.g. Zn1Ca1)
- Electrode preparation: Biocarbon particles + Carbon black + PTFE on Ni foam
- Characterizations: TEM, gas adsorption, XRD, Raman, XPS, Electrochemical tests

Results and discussion – Pore structure

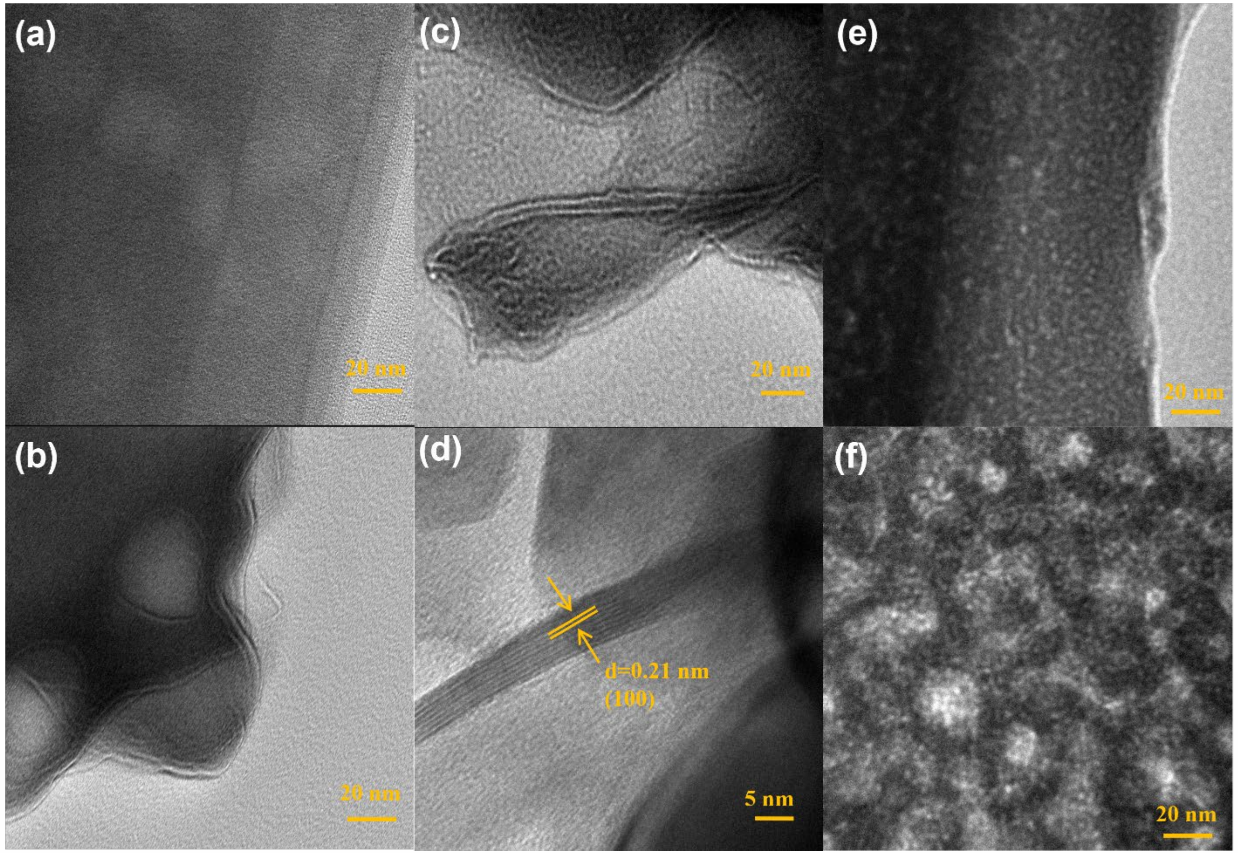


Fig. 1. HRTEM images of (a-b) Zn1Ca1, (c-d) Zn2Ca2 and (e-f) Zn4Ca4.

Pu et al. (2023). Manuscript submitted for publication.

- Zn1Ca1: Microporous structure
- Zn2Ca2: Hierarchical porous structure with substantial micropores and mesopores
- Zn4Ca4: Mesoporous structure

Results and discussion – Physical properties

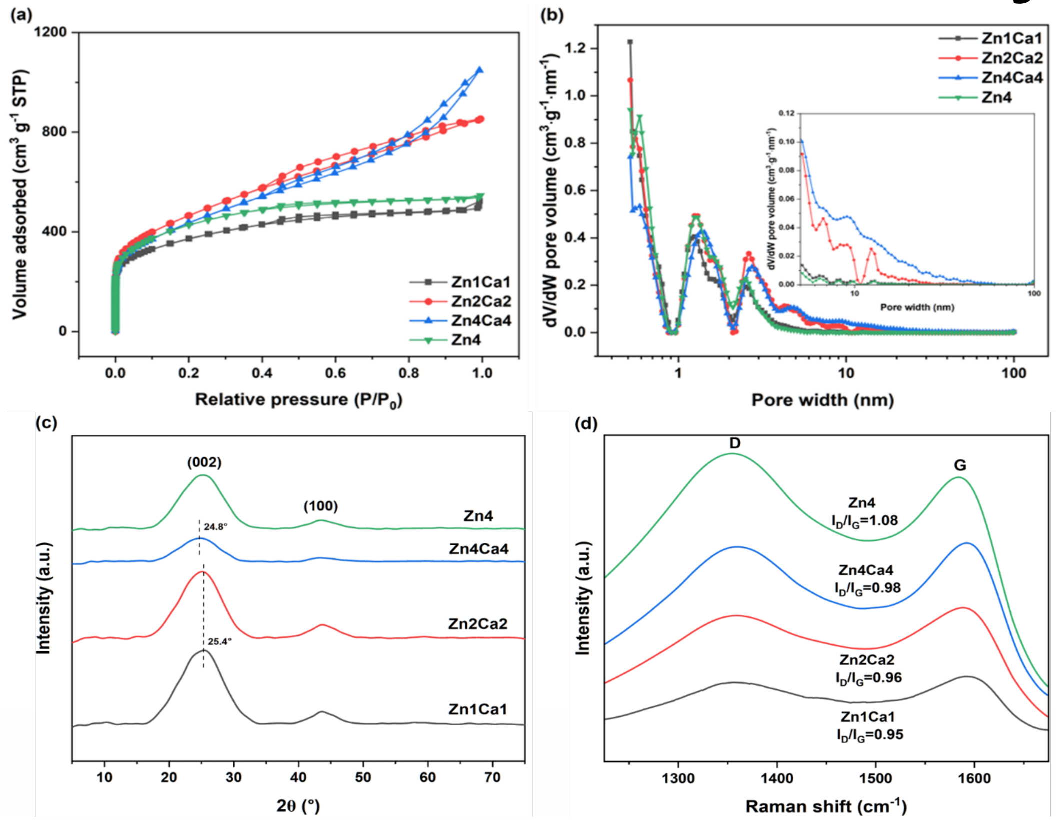


Fig. 2. (a) N_2 adsorption/desorption isotherm, (b) pore size distribution, (c) XRD diffractogram and (d) Raman spectra of Zn1Ca1, Zn2Ca2, Zn4Ca4 and Zn4.

Pu et al. (2023). Manuscript submitted for publication.

- Pore size distribution can be manipulated with more mesopores > 5 nm created under high salt loadings.
- XRD: Larger d spacing by more salts
- Raman: Higher graphitization degree by molten Zn-Ca systems

Results and discussion – Pore textures

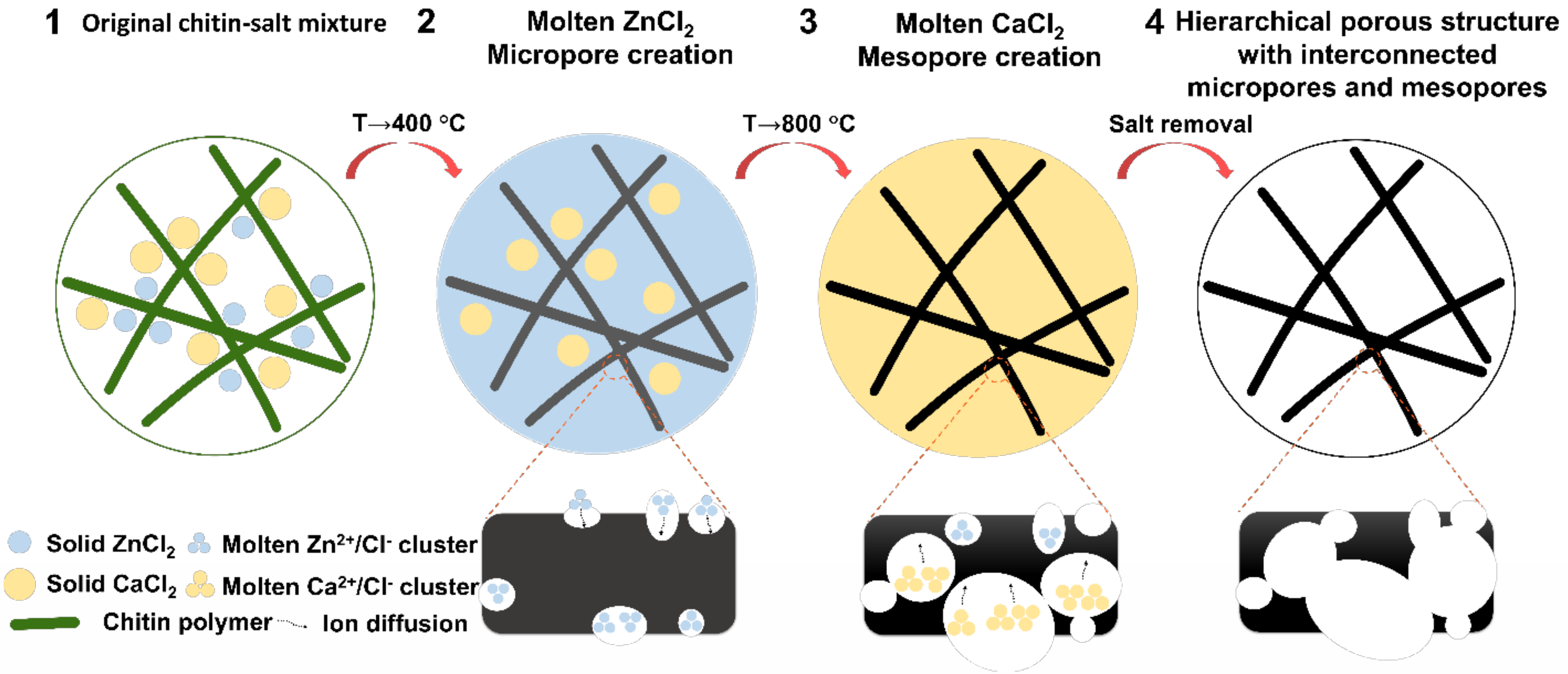
Table 1 Pore parameters of biocarbon derived from different salt ratios and systems.

Biocarbon	S_{BET}, m^2/g	V_{total}, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{meso} /V_t	d_{ave}, nm
Zn1Ca1	1338	0.81	0.65	0.16	19.3%	2.5
Zn2Ca2	1671	1.32	0.69	0.64	48.2%	3.2
Zn4Ca4	1571	1.63	0.52	1.10	67.9%	4.1
Zn4	1554	0.85	0.75	0.09	11.1%	4.1
Ca2	573	0.46	0.21	0.25	55.0%	3.2
Zn2K2	842	0.89	0.24	0.65	73.0%	3.9
Zn4K4	833	0.99	0.26	0.73	73.7%	4.8
Zn2Ca2 (leftover)	488	0.52	0.25	0.27	51.9%	4.3

- Zn2Ca2: Synergistic effect on creating well-balanced micro-mesopores
- Zn2K2: Mesopore dominated structure due to pore fusion

Pu et al. (2023). Manuscript submitted for publication.

Results and discussion – Schematics on pore formation



Ion size: Zn^{2+}: 74 pm Ca^{2+}: 100 pm Cl^-: 167 pm

Pu et al. (2023). Manuscript submitted for publication.

Results and discussion – Heteroatom doping

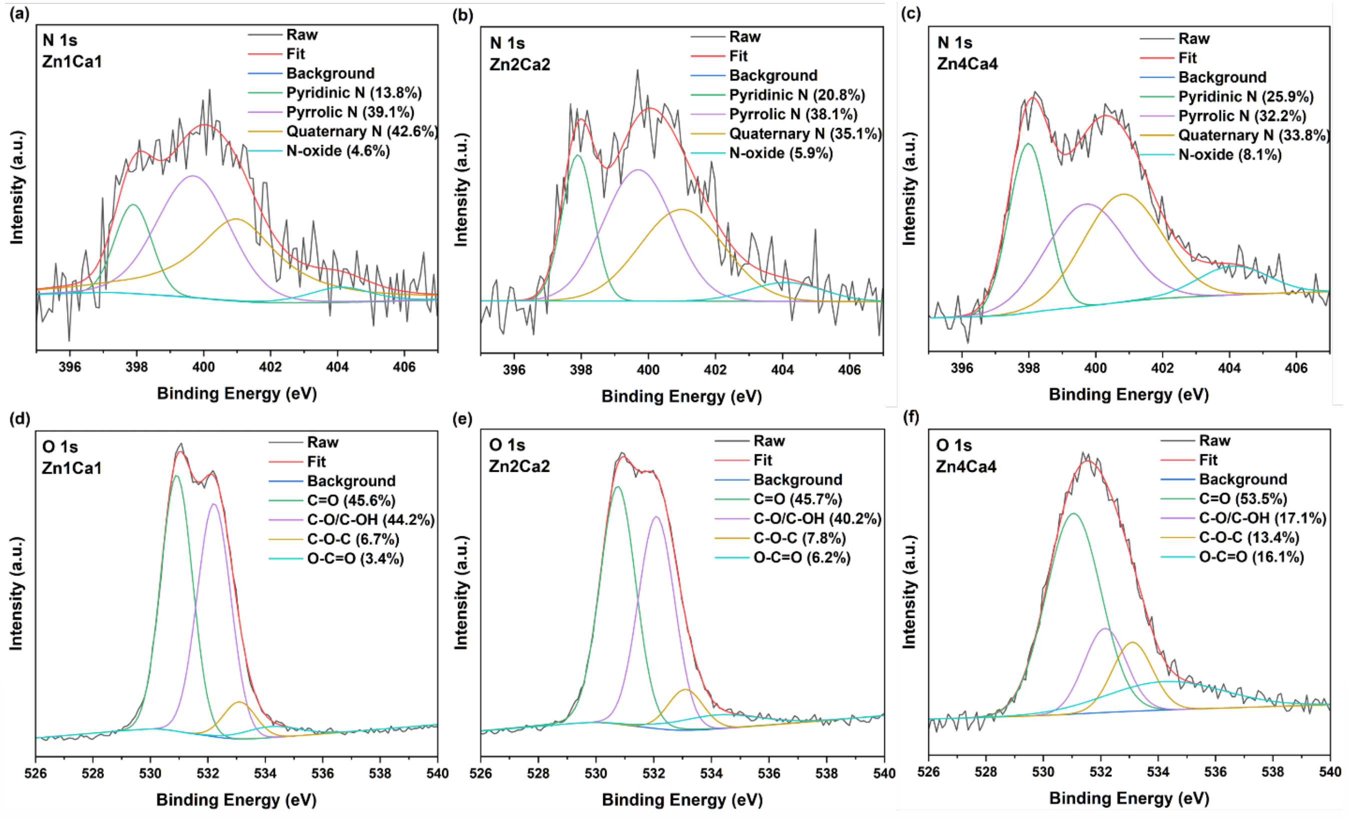


Fig. 3. High-resolution XPS spectra of (a-c) N 1s and (d-f) O 1s for Zn1Ca1, Zn2Ca2 and Zn4Ca4.

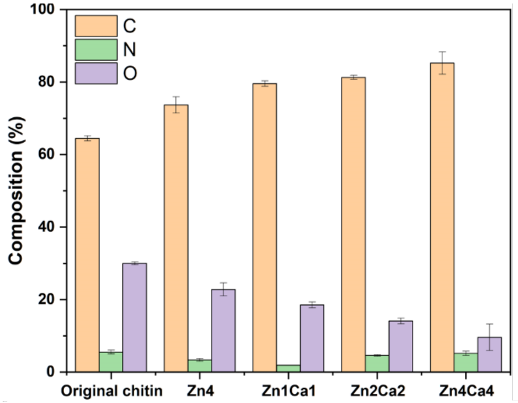


Fig. 4. Elemental composition of chitin and its derived biocarbon.

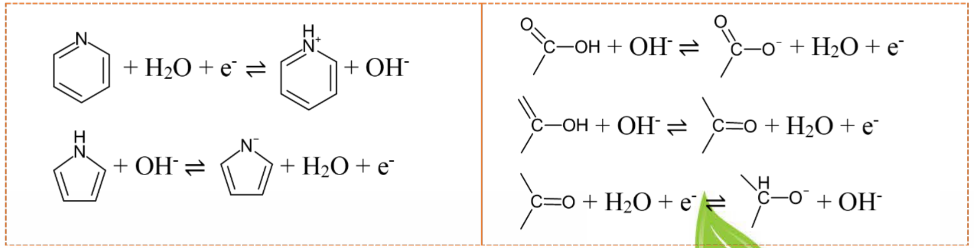
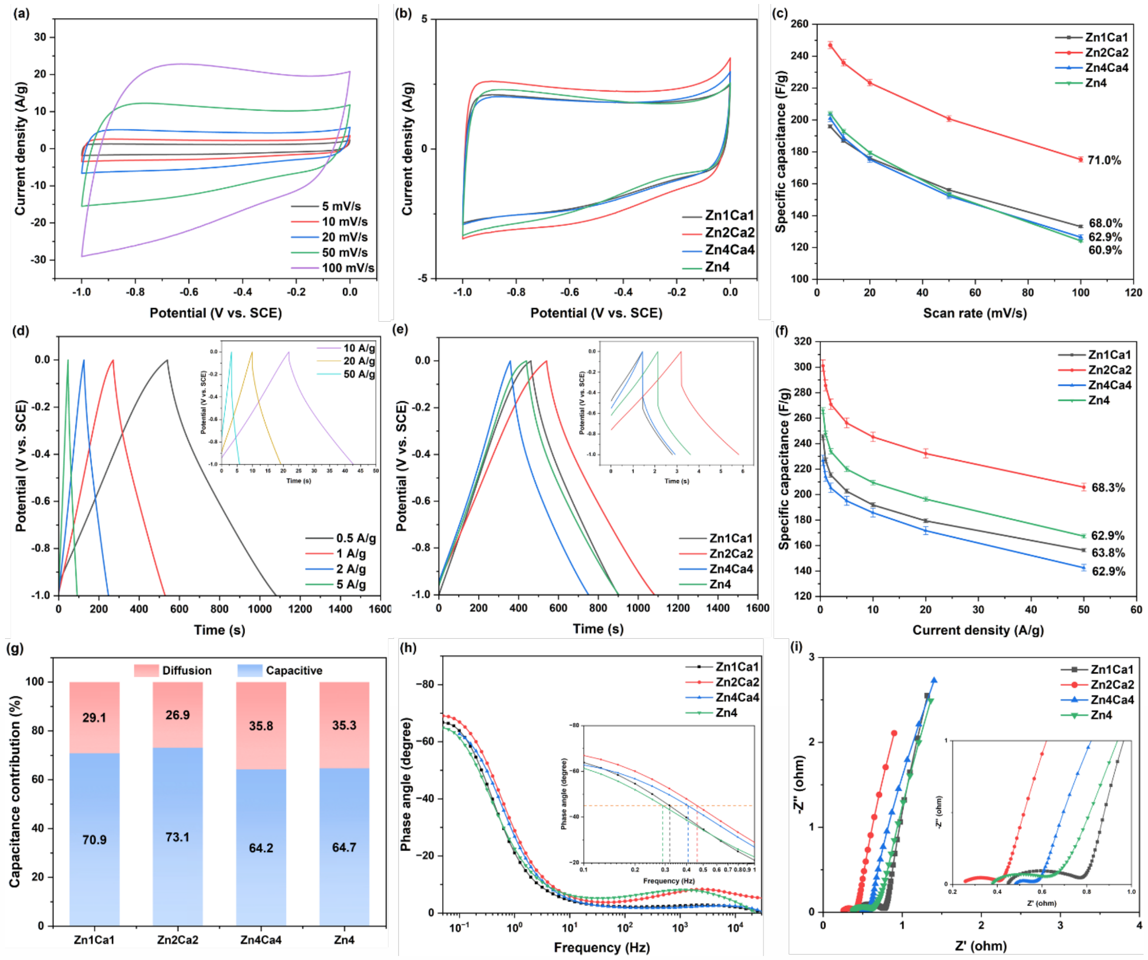


Fig. 5. Proposed Faradaic redox reactions.

Pu et al. (2023). Manuscript submitted for publication.

Results and discussion – Electrochemical tests in 3-electrode system



Pu et al. (2023). Manuscript submitted for publication.

- High specific capacitance
- Good rate capability
- Fast response
- Low internal resistance

Fig. 6. CV curves of (a) Zn2Ca2 and (b) all samples at 10 mV/s; (c) Capacitance-scan rate plot; GCD curves of (d) Zn2Ca2 and (e) all samples at 0.5 and 50 A/g (inset); (f) Capacitance-current density plot; (g) Capacitance contribution; (e) Bode plot and (f) Nyquist plot.

Results and discussion – Electrochemical tests in 2-electrode system

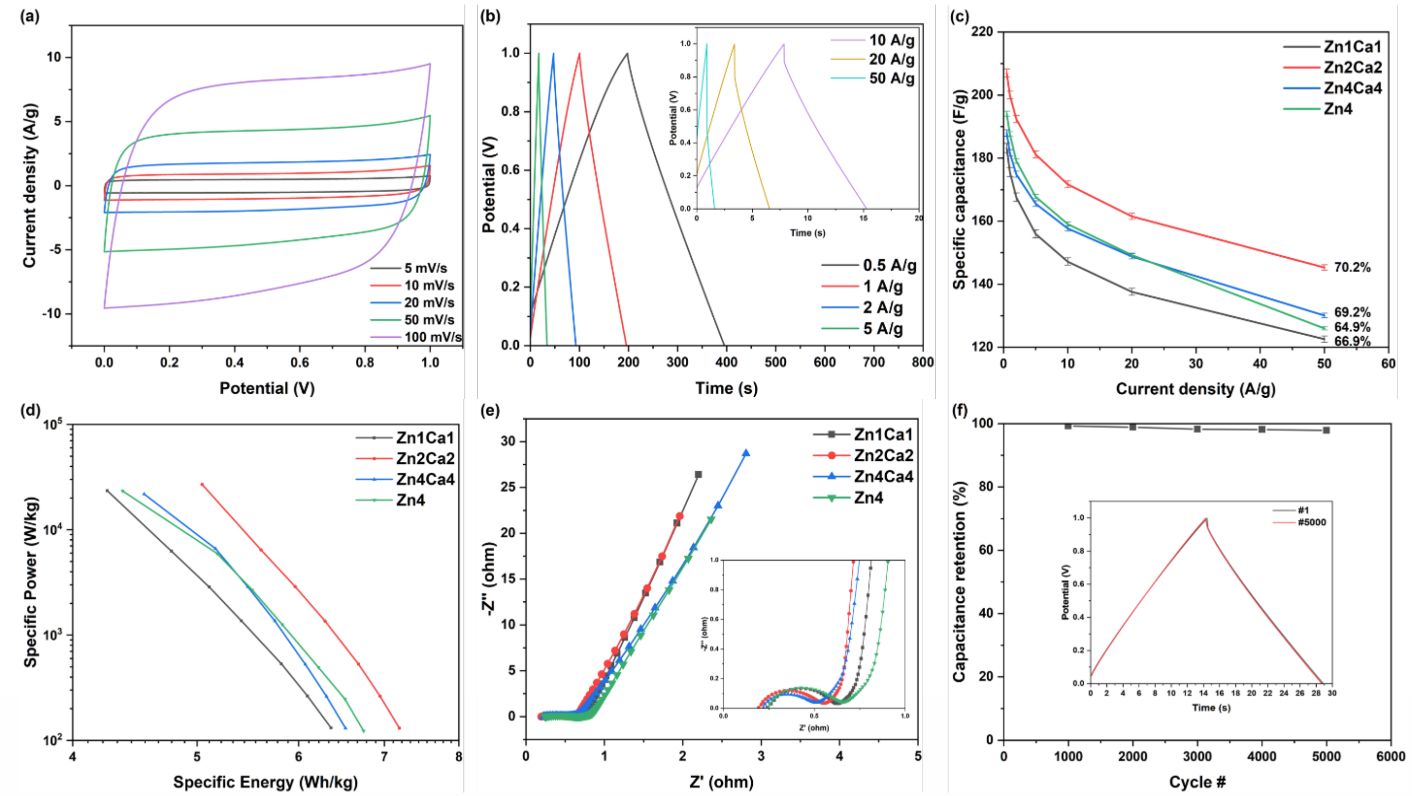


Fig. 7. (a) CV curves and (b) GCD profiles of Zn2Ca2; (c) Capacitance-current density plot; (d) Ragone plot; (e) Nyquist plot; (f) cyclic stability after #5000 cycles.

Pu et al. (2023). Manuscript submitted for publication.

- High specific capacitance
- Good rate capability
- Low internal resistance
- Outstanding power density
- Excellent cyclic stability

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Conclusion

- The binary $ZnCl_2$-$CaCl_2$ molten salt system overcame the typical limitations of traditional activation/templating strategies, while improving the micropore volume, reducing the pore fusion effect and total salt loadings compared with other $ZnCl_2$-based eutectic salt systems.

- The molten state of $CaCl_2$ was critical to further modify mesopores to achieve hierarchical porous structure.

- Zn2Ca2 showed a synergistic effect on achieving high specific surface area and creating well-balanced micro-mesopores with controllable mesopore size distribution.

- Due to the well-modulated pore structure and preserved heteroatoms of Zn2Ca2, the assembled supercapacitor cell demonstrated superior electrochemical performance.

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Thanks for listening!

Q & A