Impedance Study on Non-Faradaic Process of Hierarchical Hollow Core-Mesoporous Shell Carbon

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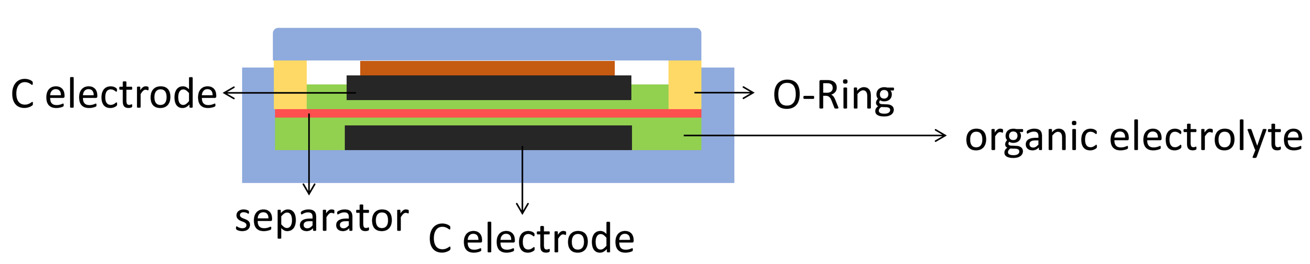
Introduction

- The complexity of the porous structure affects electron conduction, mass-transport in the pores and charge-transfer[1].
- Controlled structure of hierarchical hollow core-mesoporous shell carbon (HCMS) as supports for electrochemical applications, provides enhanced performance[2, 3].
- The objective of this study is to unveil the non-faradic and faradic process of HCMS carbon in lithium-based organic electrolyte by electrochemical impedance techniques.

Experimental

- 3D hierarchical hollow core-mesoporous shell carbon material (HCMS) was synthesized via replication of assembly of core-shell silica spheres[2].
- The electrolyte employed was 1 M $LiPF_6$ in a 1:1:1 (v:v:v) mixture of EC, DMC and EMC.
- Symmetrical cells were used for impedance tests:



Results

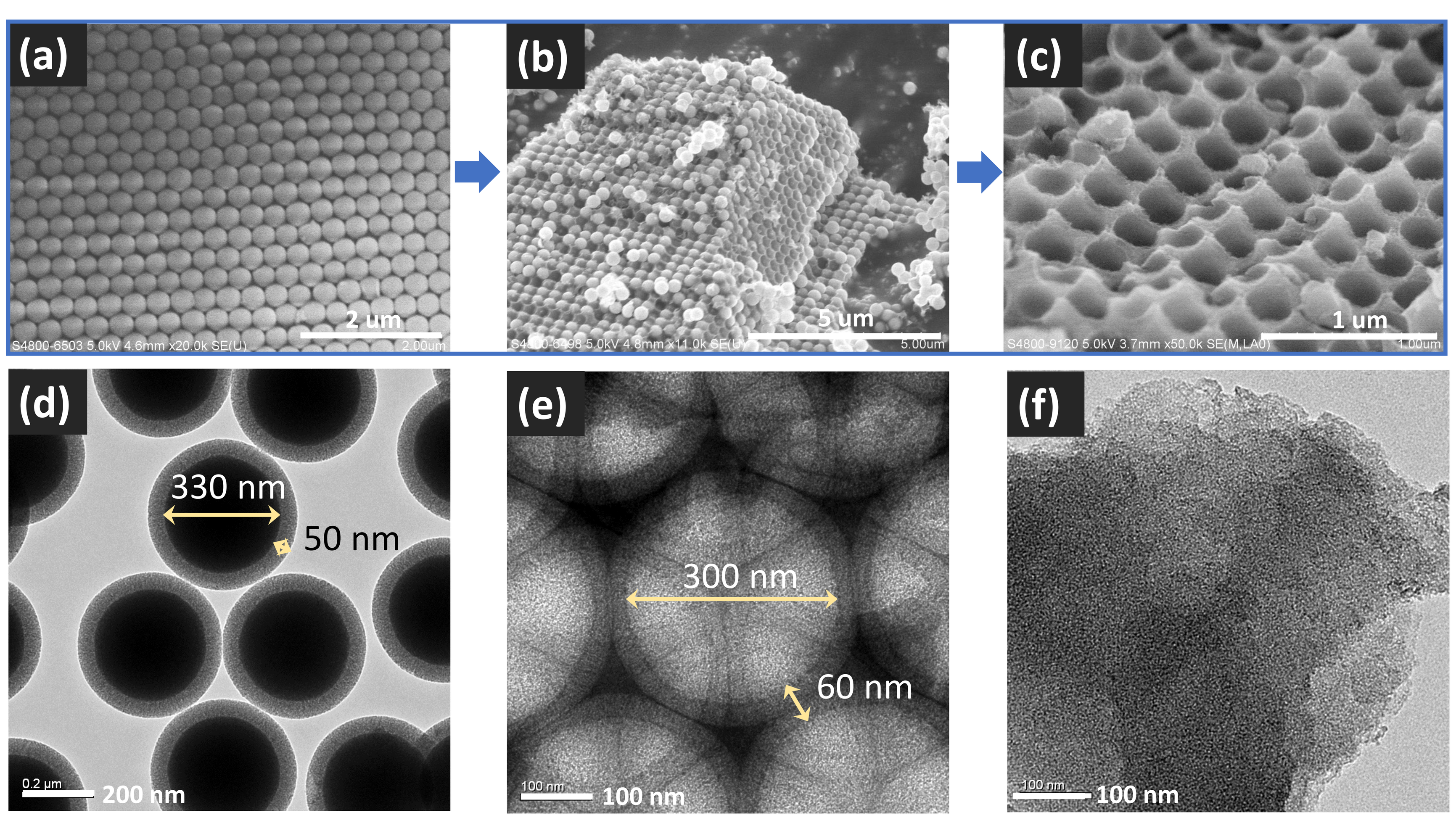


Fig. 1 SEM images of (a) core-shell silica spheres, (b) silica/carbon composite after impregnation with carbon precursor and carbonization, and (c) as-prepared HCMS material after removal of silica template. TEM images of (d) silica spheres, (e) HCMS material, and (f) supercapacitor grade activated carbon (AC).

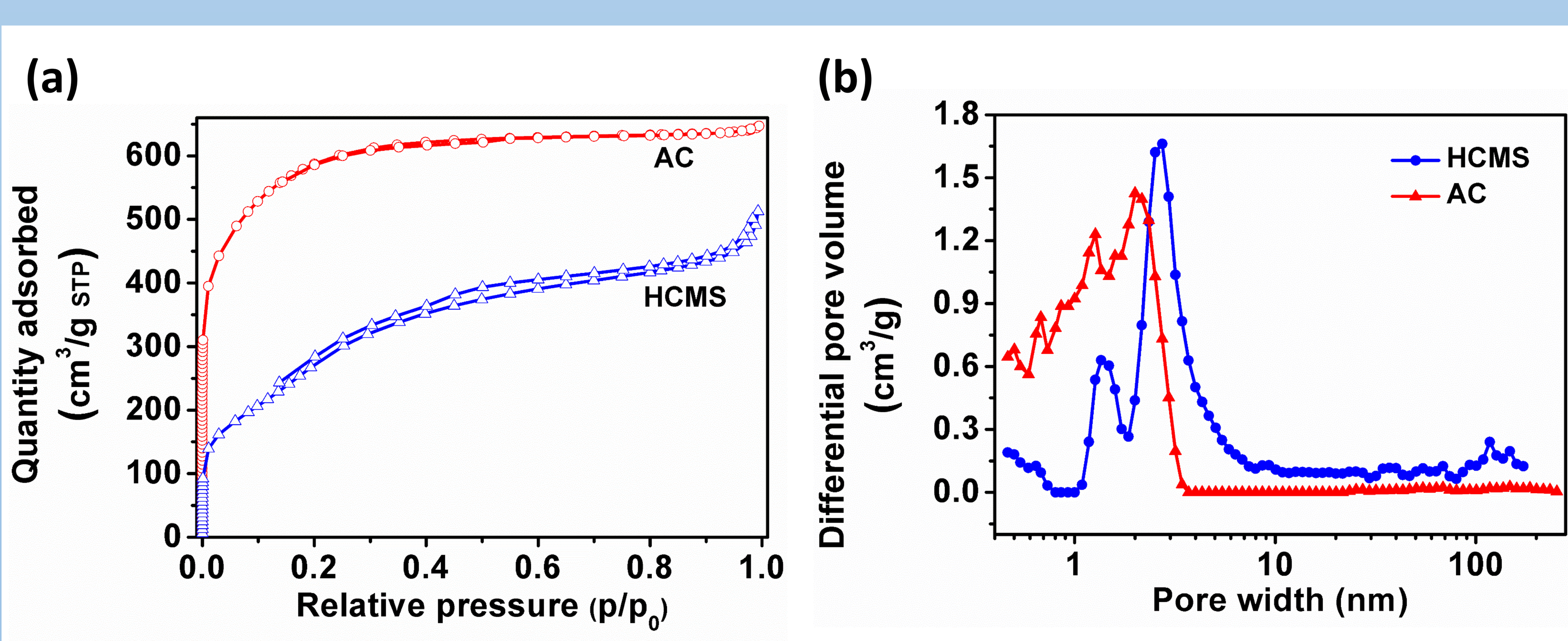


Fig. 2 (a) N_2 sorption isothermals, and (b) DFT pore size distribution curves for HCMS and AC materials.

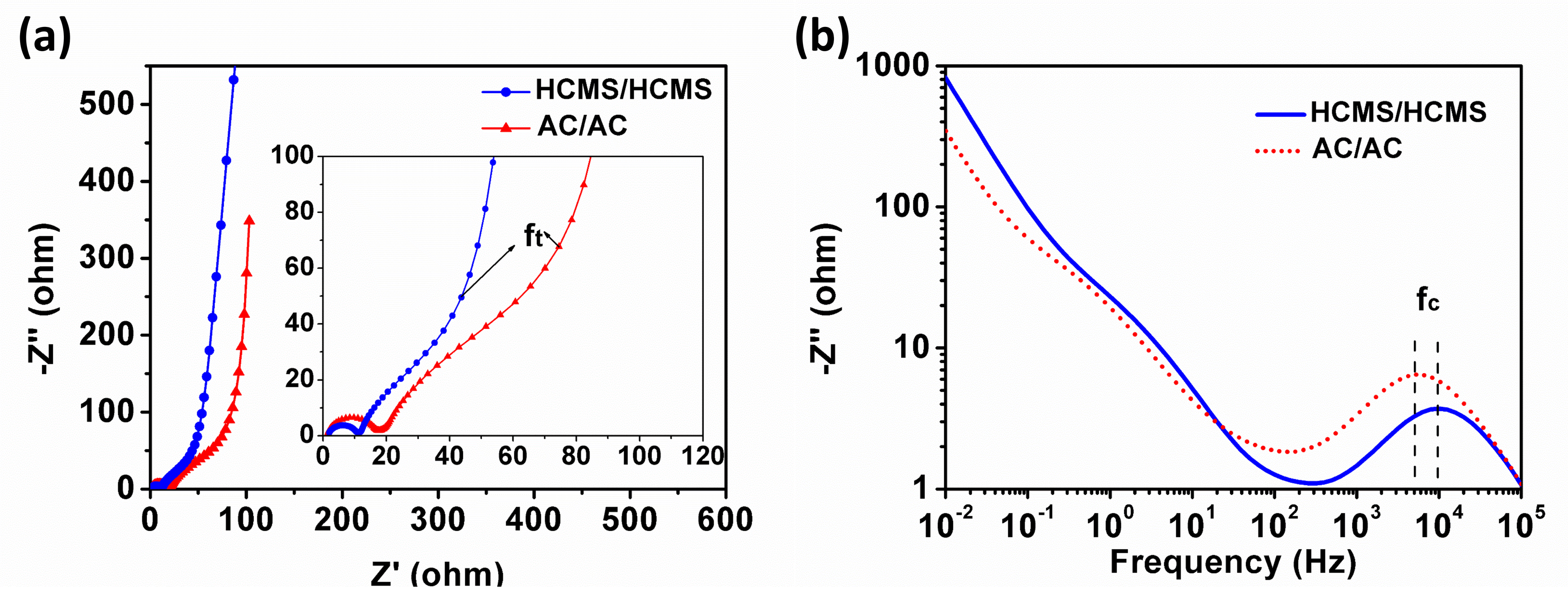


Fig. 3 (a) Nyquist plots, and (b) curves of imaginary part versus frequency for symmetrical HCMS/HCMS and AC/AC cells.

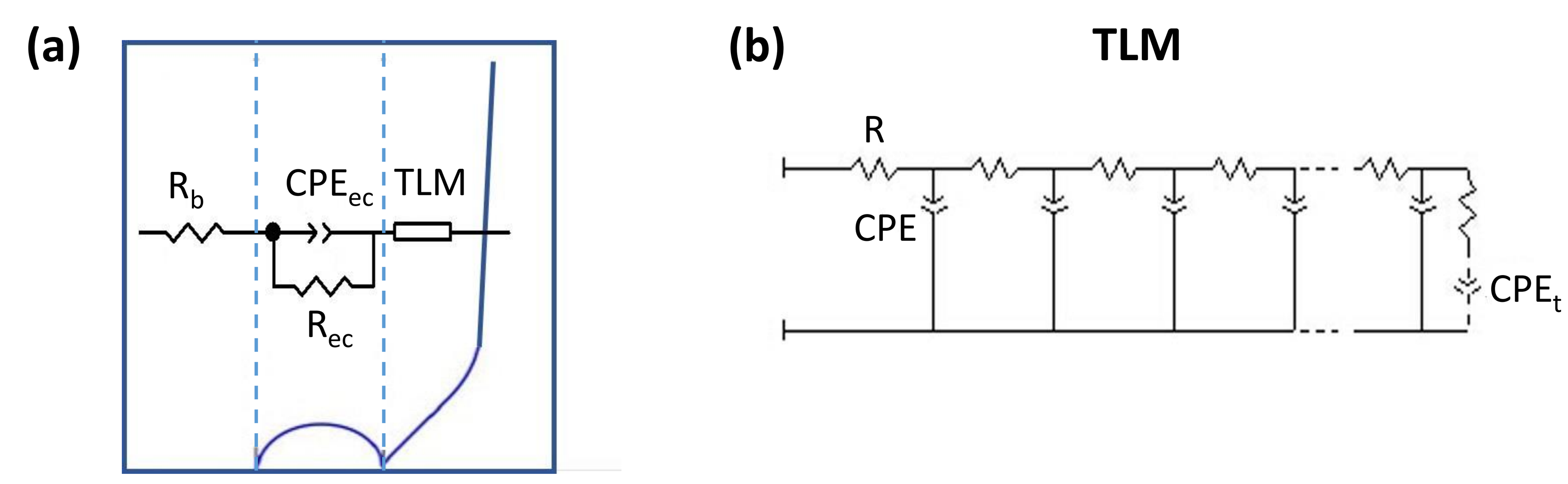


Fig. 4 (a) Equivalent circuit model used for impedance fitting, and (b) transmission line model (TLM).

Table 1 Impedance parameters of symmetrical HCMS/HCMS and AC/AC cells

	R_b/Ω	R_{ec}/Ω	τ_{ec}/s	N	$R_{pore\text{-}total}/\Omega$
HCMS/HCMS cell	1.6	9.3	$1.56*10^{-5}$	3	84.3
AC/AC cell	1.4	15.2	$3.16*10^{-5}$	5	184.3

R_b: resistance of bulk electrolyte
R_{ec}, τ_{ec}: resistance and time constant of electron conduction process
N: number of TLM branches
$R_{pore\text{-}total}=\sum R_{pore\text{-}n}$ (n=1, 2…, N), which reflects resistance of ions diffusion in pores

Conclusions

- 3D hierarchical carbon framework with hollow core, mesoporous shell was synthesized.
- In lithium organic electrolyte, the Nyquist plot shows typical characteristic of porous electrode for HCMS carbon. One semicircle corresponds to electron conduction process; and an inclined -45° line followed by a nearly vertical line is observed to reflect ion diffusion inside pores.
- Controlled bimodal HCMS structure has smaller resistance of ion diffusion in pores. Probably due to the unique hierarchical nanostructure facilitating effective ion transfer.
- Extensive work in other electrolytes is still on-going.

References

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2. F. Li, et al. Journal of Materials Chemistry, 2011, 21, 8880.
3. M. Zhou, et al. Advanced Energy Materials, 2014, 4.

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