Highly Active and Stable Iron-nitrogen-doped Carbon with Hollow-core-mesoporous-shell (HCMS) Structure for Oxygen Reduction Reaction

*Ming Zhou, Kwong-Yu Chan**

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

***Corresponding author Email:** hrsccky@hku.hk*

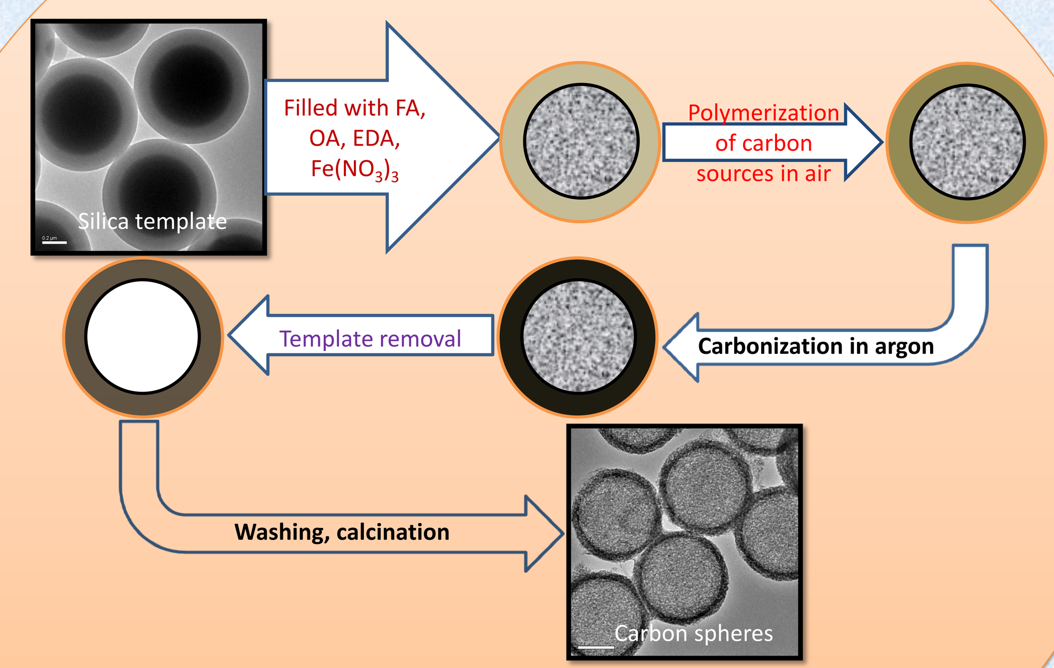
❖**ORR issue**: fuel cells; rechargeable metal-air batteries.

❖**Problems**: mass-transport limitation; high costs; degradability of electrocatalysts.

❖**Solution**: non-precious metal and nitrogen doped carbons; low costs, good electrochemical activity, and durability.

❖**HCMS**: high surface area; large pore volume; multi-scale porosity; enhanced mass transfer.

❖**Motivation**: combination of the high activity of iron-nitrogen-doped carbon (Fe-N-C) and the fast transport provided by the hierarchical porosity of a uniform hollow-core mesoporous-shell (HCMS) structure.



Scheme 1. Experimental procedure for the synthesis of Fe-N-HCMS. **FA** furfuryl alcohol; **OA** oxalic acid; **EDA** ethylenediamine

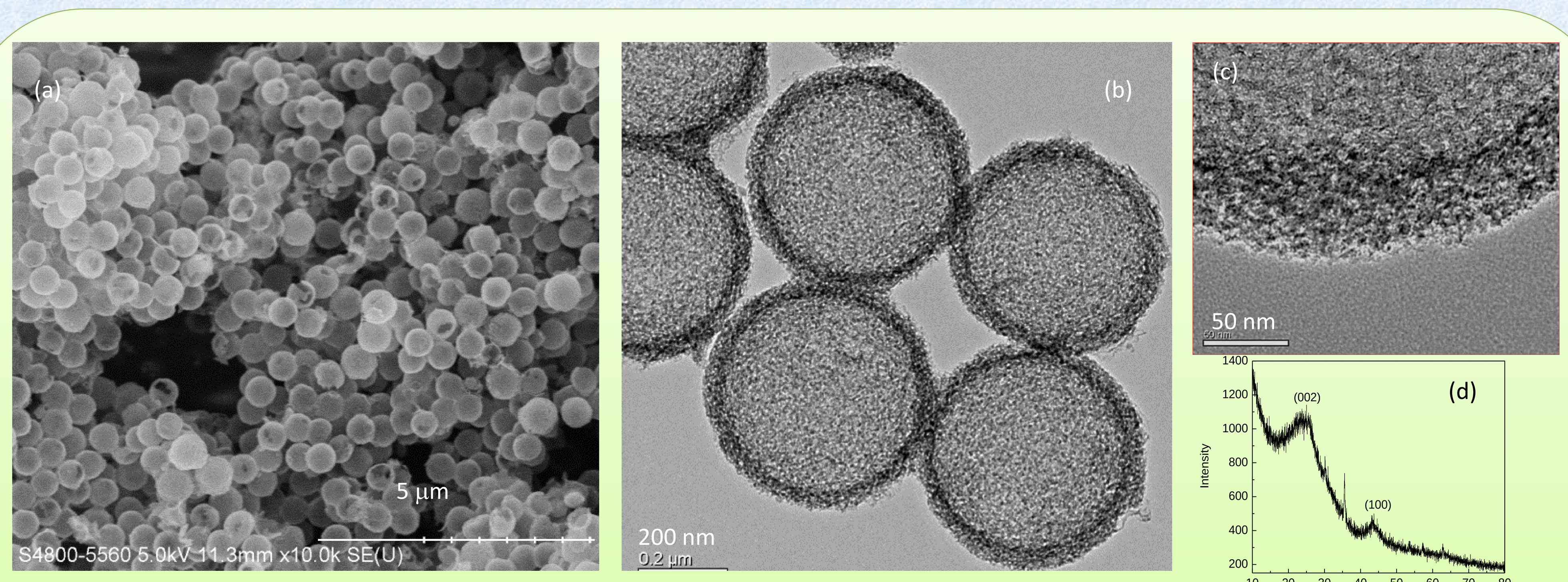


Figure 1. SEM image (a), TEM image at low magnification (b), TEM image at high magnification (c) and the XRD pattern (d) of the synthesized Fe-N-HCMS.

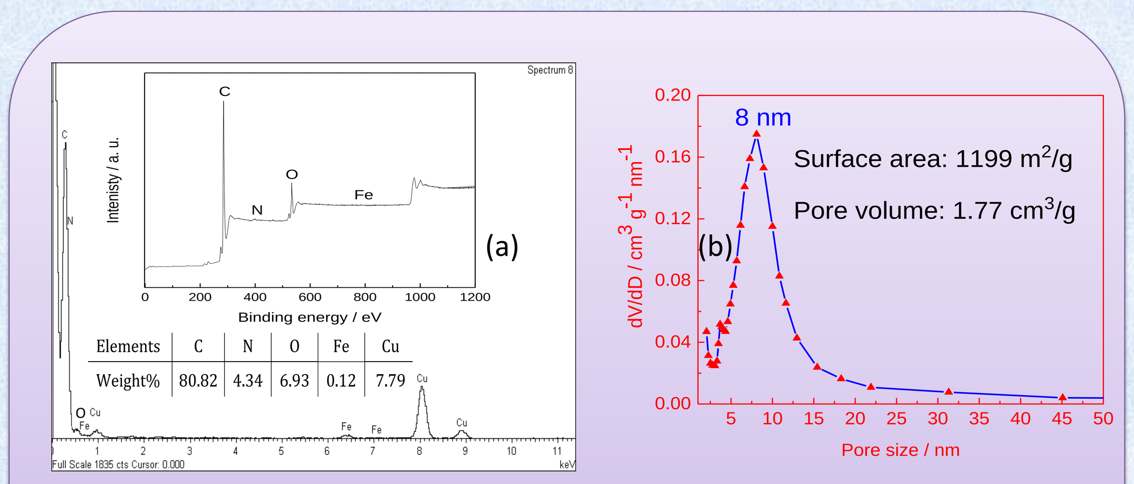
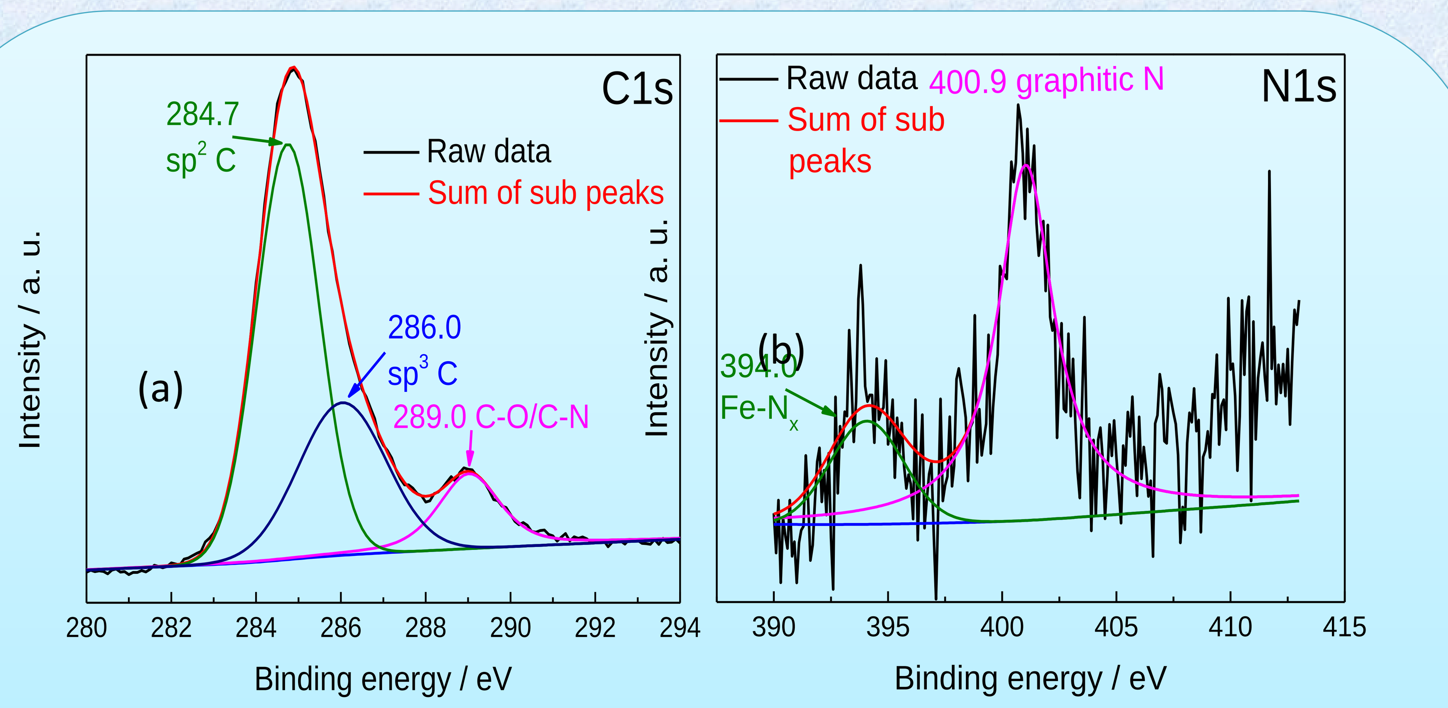


Figure 2. EDX results and corresponding long range XPS spectrum (a), nitrogen sorption pore size distribution, surface area, and pore volume of Fe-N-HCMS (b).



The Fe content was too low to be quantified accurately by EDX and XPS, it was analyzed to be 0.75% m/m by ICP-AES. The amount of iron is on the low side of previously reported values of Fe-N doped carbon, but is crucial for ORR by forming $Fe-N_x$ active sites and inducing favorable N-C lattice structures.

Figure 3. XPS carbon spectrum (a) and nitrogen spectrum (b) of Fe-N-HCMS.

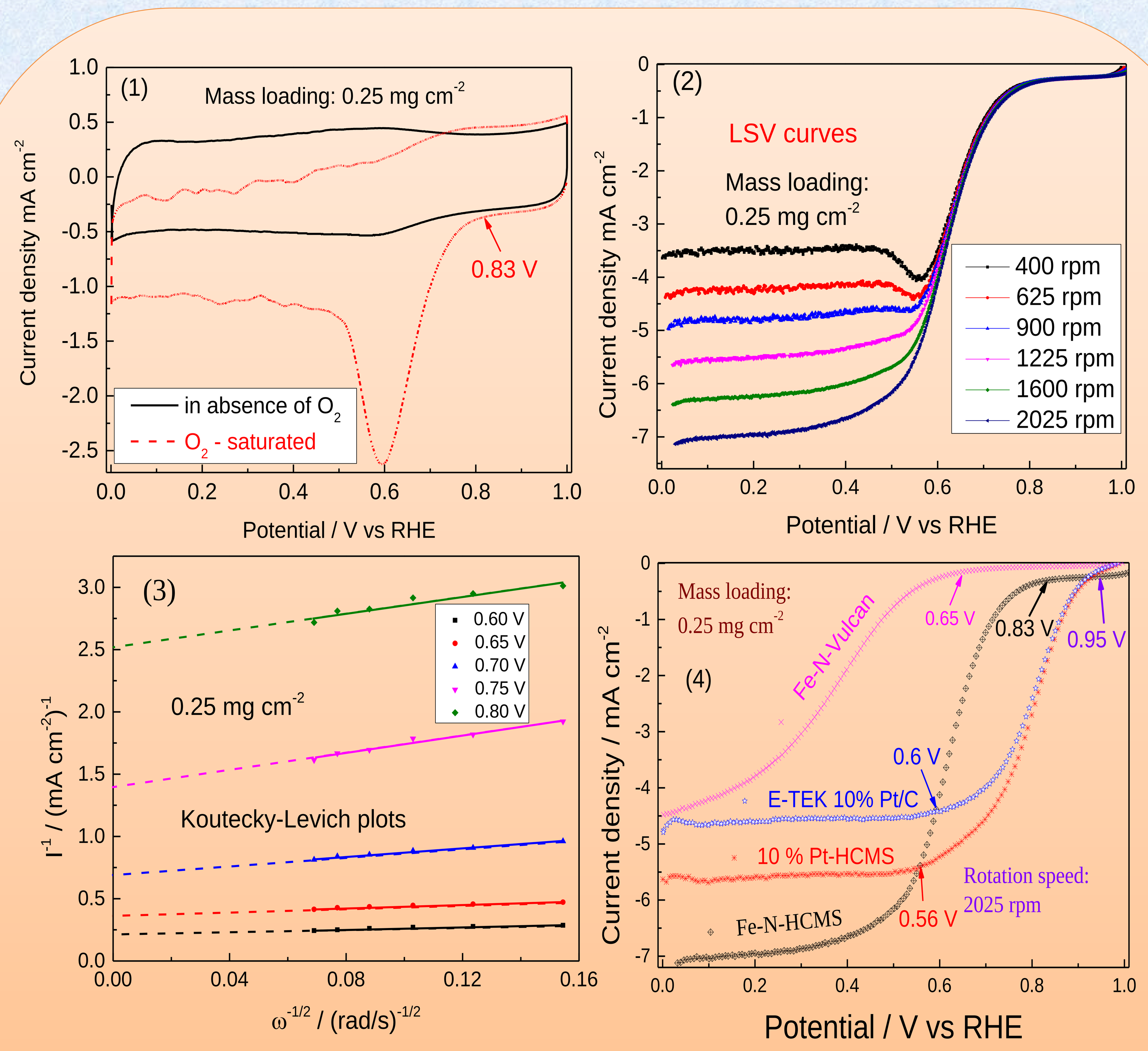


Figure 4. CV scans in presence and absence of oxygen (1), LSV at different rotation speeds (2) and corresponding Koutecky-Levich plots (3) of Fe-N-HCMS; LSV curves of the four electrocatalysts: Fe-N-Vulcan, E-TEK Pt/C, Pt-HCMS, and Fe-N-HCMS (4). Scan rate: 10 mV/s; electrolyte: 0.5 M H_2SO_4.

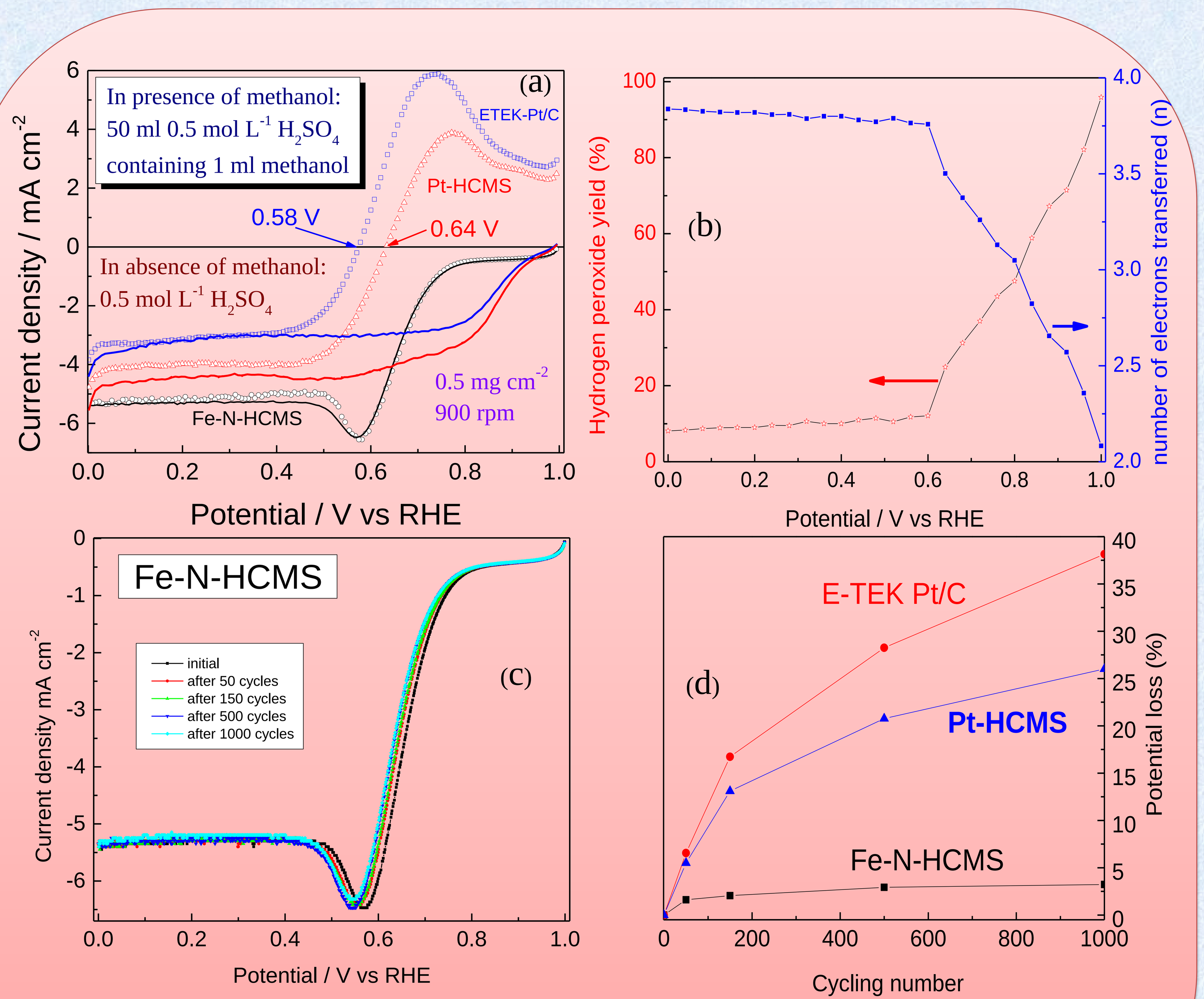


Figure 5. Tolerance of ORR to methanol (a), transferred electron numbers and hydrogen peroxide yield (b) and durability tests (c) of Fe-N-HCMS, comparisons of stability between Fe-N-HCMS and two Pt electrocatalysts (d). 10 mV/s in 0.5 M H_2SO_4 with mass loading of 0.5 mg/cm^2

In conclusion, the synthesized Fe-N-HCMS demonstrates: **(i)** a high onset potential (0.83 V); **(ii)** high limiting current densities (-7.0 mA/cm^2 at 2025 rpm); **(iii)** high tolerance to methanol; **(iv)** high stability (< 4% potential loss); **(v)** four-electron mechanism (3.8 electrons transferred). The excellent performance can be attributed to: (a) well developed active sites ($Fe-N_X$); (b) HCMS structure (enhanced mass-transfer, high surface area for charge transfer, mechanical strength, and resistance to degradation).

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