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# Novel porous carbon material derived from hypercross-linked polymer of p-xylene for supercapacitors electrode

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## ABSTRACT

Herein, we report for the first time the synthesis of porous carbon which is derived from hypercross-linking of p-xylene through Friedel-Crafts alkylation and subsequent carbonization at 800 °C for supercapacitor applications. The formation of hypercross-linking in p-xylene was confirmed by Fourier transform infra-red (FT-IR) spectroscopy. The synthesized materials, hypercross-linked p-xylene (HCP-pXy) and pyrolyzed HCP-pXy (HCP-pXy-800) were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen sorption isotherm and powder x-ray diffraction (XRD) pattern. In a three-electrode system, HCP-pXy-800 electrode showed a specific capacitance of 242.5 F g<sup>-1</sup> at a current density of 1.25 A g<sup>-1</sup> in a 3 M KOH aqueous electrolyte. Furthermore, the specific capacitance at a current density of 1.25 A g<sup>-1</sup> remained 95.18% after 2000 charge-discharge cycles and thus illustrating a predominant cyclic stability of the p-xylene derived porous carbon electrode.

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## 1. Introduction

Supercapacitors (SCs) have received remarkable consideration in the renewable energy storage field because of their long cycle life, adequate power density and rapid rate of charge-discharge [1]. Also, SCs serve as a barrier between capacitors and batteries and can be divided into three subcategories: (i) Electric double layer capacitor (EDLC), (ii) pseudocapacitor and (iii) battery supercapacitor hybrid (BSH) [2]. To date, different carbonaceous materials derived from activated carbon [3] and biowaste [4,5] were successfully studied as an electro-active material in EDLC owing to their huge surface area, porosity and comparatively low-cost. However, the main drawback associated with those biomass-derived carbons is that a chemical activation process such as KOH, ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> is required to activate the carbon derived-biomass [6]. Recently, hypercross-linked polymers (HCPs) derived porous carbons are considered as one of the most alternative products for supercapacitor applications [7–10] owing to their high surface area, specific porosity, good physical and adequate chemical stability, excellent selectivity and structural diversity.

p-Xylene (*para*-xylene) is one of the three isomers of dimethylbenzene and is collectively known as xylenes. The p-xylene is an aromatic hydrocarbon. Herein, we adopt a two-step methodology to construct porous carbon via hypercross-linking of p-xylene followed by carbonization. The fabricated electrode material delivers a specific capacitance of 242.5 F g<sup>-1</sup> at 1.25 A g<sup>-1</sup> without the use of chemical activation process. These interesting outcomes demonstrate the ability to prepare supercapacitor electrode materials with a superior and efficient performance.

## 2. Experimental

### 2.1. Synthesis of hypercross-linked polymer of p-xylene

1.0 g of p-xylene and 0.5 g of dimethoxy methane were added to 20 mL of 1,2-dichloroethane in a 100 mL round bottom flask provided with magnetic stirrer. After stirring the mixture for 30 min, 3.0 g of ferric chloride was added to it under stirring. Then, the reaction was subjected into 24 h at 80 °C. Finally, the brown colored sediment was continuously washed with enormous amount of water, ethanol and acetone mixture. Finally, the obtained hypercross-linked polymer of p-xylene was dried in hot-air oven at 100 °C for 12 h and designated as HCP-pXy.

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## 2.2. Carbonization of HCP-pXy

A known quantity of HCP-pXy was kept in tubular furnace under helium atmosphere for 5 h at 800 °C with the heating rate of 2 °C min<sup>-1</sup>. The schematic illustration of the reaction scheme was shown in Fig. 1. The materials, physicochemical characterization techniques and the fabrication of working electrode are depicted in supporting information section.

## 2.3. Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were studied by using Biologic SP150 electrochemical workstation. Nickel foam was used as the substrate material to fabricate the working electrode. Platinum wire and Ag/AgCl were used as the counter and reference electrode, respectively. The specific capacitance was calculated from the GCD curve using the following equation:

$$C_s = \frac{I\Delta t}{m\Delta V}$$

where,  $C_s$  is the specific capacitance of the HCP-pXy-800 electrode (F g<sup>-1</sup>),  $I$  is the given current (A),  $\Delta t$  designates the discharge time (s),  $m$  represents the weight of the active material (g) and  $\Delta V$  is the potential window (V).

## 3. Results and discussion

The FTIR spectrum of hyper cross-linked polymer of p-xylene was shown in Fig. 2(a). It shows a broad band about 3450 cm<sup>-1</sup> which

is due to hydrogen bonded -OH groups formed by the hydrolysis of residual uncondensed end methoxy groups of the product. The peak at 2917 cm<sup>-1</sup> accounts for methyl groups, quinonoid hydrogens and aromatic ring hydrogens. The coupled vibrations of quinonoid C=C bond yielded an intense peak at 1682 cm<sup>-1</sup>. It is a characteristic one for the formation of hyper cross-linked conjugated quinonoid. The sharp shoulder peak at 1612 cm<sup>-1</sup> is due to C=C vibration of aromatic rings. The -CH<sub>3</sub> bending vibrations occurred at 1378 and 1449 cm<sup>-1</sup>. The alcoholic C-O vibration showed a peak at 1032 cm<sup>-1</sup>. The aromatic ring skeletal vibration yielded its sharp peak at 885 cm<sup>-1</sup>. The =CH- bending vibration of quinonoid occurred at 1261 cm<sup>-1</sup>. Fig. 2(b) illustrates the XRD pattern of HCP-pXy and HCP-pXy-800. HCP-pXy exhibits only one diffraction peak at around 23°, whereas pyrolyzed material (HCP-pXy-800) displays two major diffraction peaks centered at 23° and 45° corresponding to (0 0 2) and (1 0 0) reflection planes, respectively, with slight shift. It persuasively proves the amorphous nature of the carbonized materials. The nitrogen adsorption-desorption isotherms of HCP-pXy and HCP-pXy-800 (Fig. 2(c)) exhibits type IV hysteresis which illustrates the existence of mesoporous structure. The BET surface area was found to be 352 and 489 m<sup>2</sup> g<sup>-1</sup> for HCP-pXy and HCP-pXy-800, respectively. The high specific surface area of the carbonized material due to high temperature can effectively enhance activation stability [11]. In the Raman spectrum of Fig. 2(d), the peaks around 1352 cm<sup>-1</sup> (D-band) are related to a disordered diamond-like carbon structure, whereas the peaks located at around 1585 cm<sup>-1</sup> (G-band) are accredited to an ordered carbon cluster. The I<sub>D</sub>/I<sub>G</sub> value indicates the number of defects in the ordered carbon clusters of the HCP-pXy-800 and it was found to be 1.162.

Fig. 3 shows the SEM, TEM and SAED images of HCP-pXy and HCP-pXy-800. The SEM images with different magnifications of HCP-

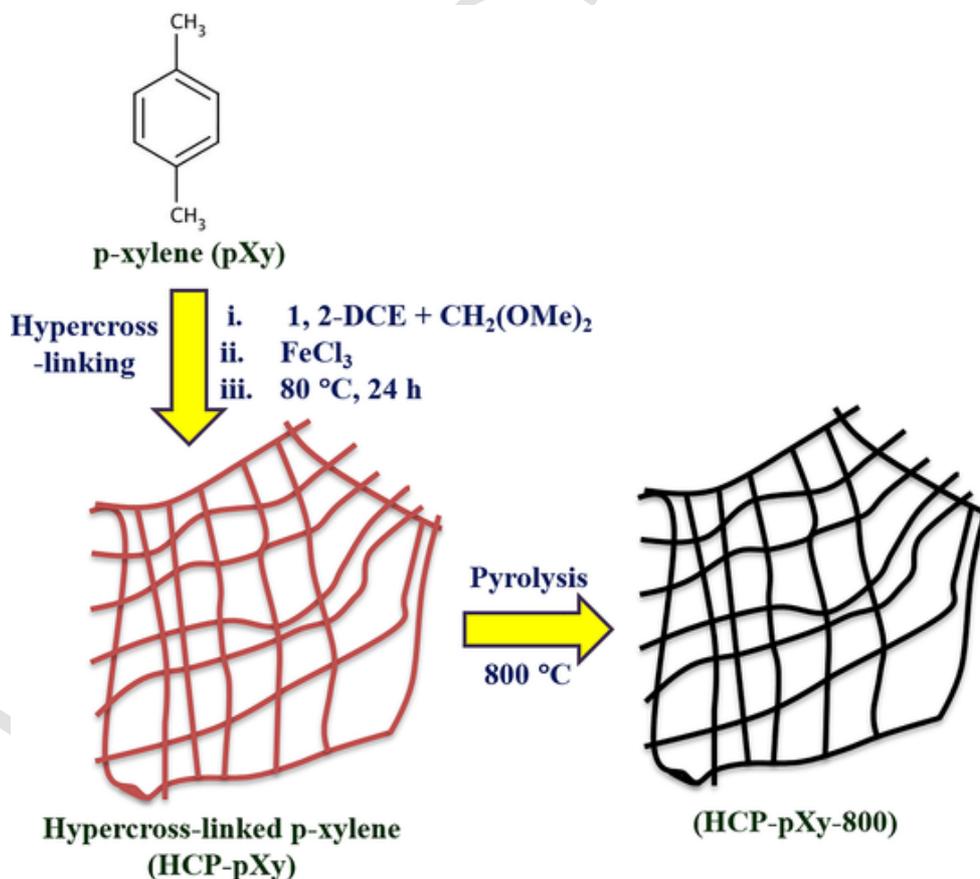


Fig. 1. Schematic illustration of the synthesis of hypercross-linked polymer of p-xylene and subsequent pyrolysis.

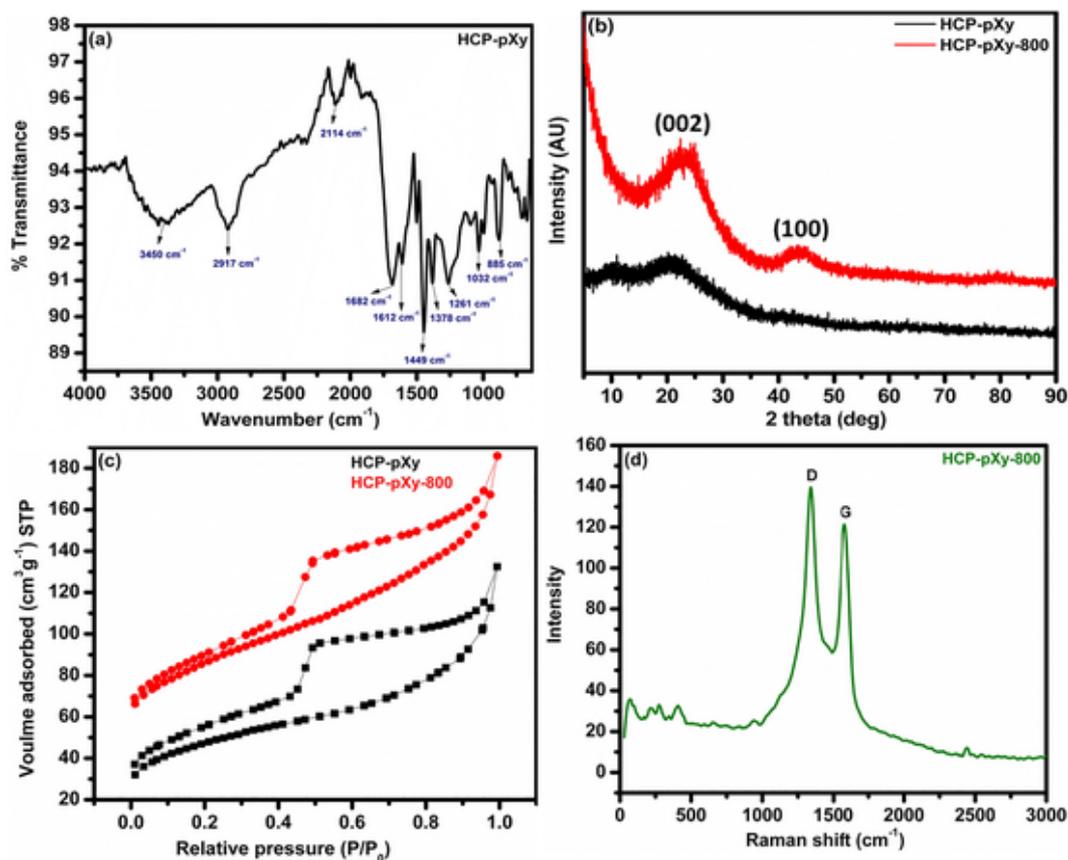


Fig. 2. (a) FT-IR spectrum, (b) XRD pattern, (c) nitrogen sorption isotherm and (d) Raman spectrum of the synthesized materials.

pXy disclose that the particles are spherical in shape with porous nature and that their sizes differ several micrometers into nanometers, which is in good agreement with the obtained TEM images. After pyrolysis at 800 °C, HCP-pXy-800 shows a hierarchical porous structure with substantial mesopores and macropores, which can provide a high speed channel to facilitate the rapid diffusion of ions. Further, the TEM image also confirms that the HCP-pXy-800 material possesses combination of mesopores and macropores. The SAED pattern confirms the amorphous nature of the HCP-pXy and HCP-pXy-800 material.

Given the advantage of high surface area and hierarchical pore structure, the HCP-pXy-800 material could be crucial in producing promising electrode materials for supercapacitors. To evaluate the supercapacitive performance of the synthesized material, CV, GCD and EIS were executed with a three electrode system in 3 M KOH aqueous electrolyte. As depicted in Fig. 4(a), the CV curve has nearly a rectangular shape with fast current response, suggesting that the prepared electrode material possesses electric-double layer capacitance (EDLC) behavior. The galvanostatic charge-discharge curves were shown in Fig. 4(b). HCP-pXy-800 exhibits almost linear and symmetrical GCD curves. It clearly demonstrates a highly reversible adsorption-desorption of electrolyte ions in the skeleton of HCP-pXy-800 electrode. The specific capacitance calculated from GCD of HCP-pXy-800 at different current densities were shown in Fig. 4(c). The maximum specific capacitance was found to be 242.5 F g<sup>-1</sup> at a current density of 1.25 A g<sup>-1</sup>. The electron-ion transport process of the HCP-pXy-800 was further investigated and the Nyquist plot was shown in Fig. 4(d). The small semicircle in the high frequency region and vertical line in the low-frequency region indicate that the charge transfer and ion diffusion speed are high enough at the materials surface. Further, the stability of the electrode material was investigated in GCD cyclic test at 1.25 A g<sup>-1</sup> for 2000 cycles (Fig. 4(e)). The HCP-pXy-800 electrode can retain

95.18% of the initial specific capacitance after 2000 cycles, suggesting excellent electrochemical stability. The inset of Fig. 4(e) shows the SEM image of HCP-pXy-800 electrode after the GCD cyclic stability test. It is clearly shown in that figure that the morphology of the sample was not much altered even after 2000 cycles. This clearly implies the stability of the synthesized electrode material. Further, EIS study was conducted after the GCD stability test. As presented in Fig. 4(f), the Nyquist plots imply negligible changes in the resistance after the stability test which clearly illustrates that the prepared electrode material, HCP-pXy-800 can retain almost unchanged electronic and ionic transport properties after 2000 cycles.

#### 4. Conclusions

We successfully synthesized a novel electrode material from p-xylene by a two-step methodology via. hypercross-linking and pyrolysis at 800 °C. The formation of hypercross-linking was confirmed by FT-IR. The surface area and porous nature of the samples were confirmed by nitrogen sorption isotherm. The surface morphology and hierarchical porous structure were confirmed by SEM and TEM techniques. In a three-electrode system, the maximum specific capacitance was found to be 242.5 F g<sup>-1</sup> at 1.25 A g<sup>-1</sup>. We strongly believe that the present electrode material can open new avenue for the future energy storage applications.

#### CRedit authorship contribution statement

**Sang-Hyo Kim:** Data curation, Writing - original draft. **Rajangam Vinodh:** Data curation, Writing - original draft. **Chandu V.V. Muralee Gopi:** Conceptualization, Methodology. **Venkata Guru Raghavendra Kummara:** Conceptualization, Methodology. **Sangaraju Sambasivam:** Writing - review & editing. **Ihab M. Obaidat:** Writing - review & editing. **Hee-Je Kim:** Supervision, Visualization, Investigation.

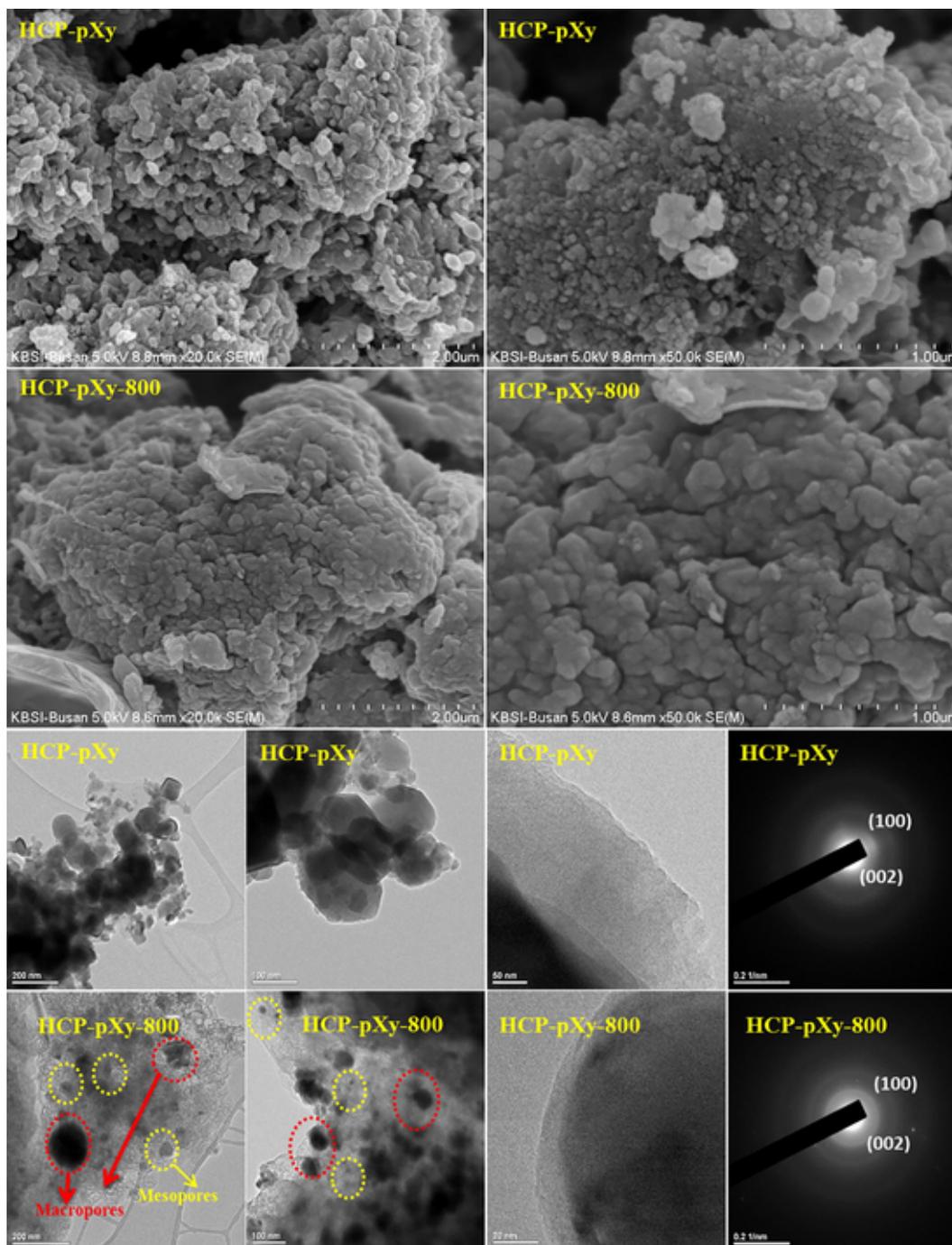


Fig. 3. FE-SEM, TEM and SAED images of HCP-pXy and HCP-pXy-800.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.127222>.

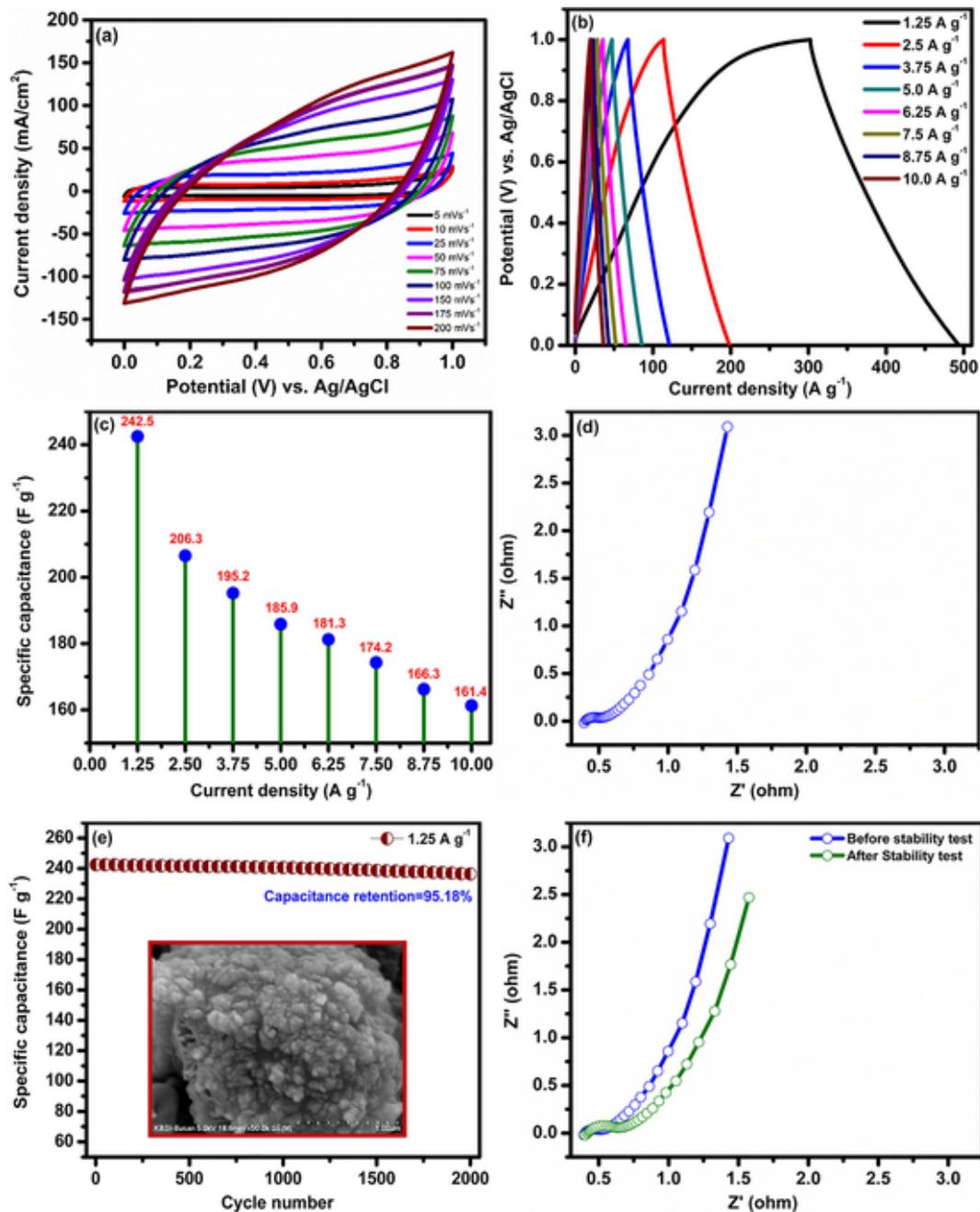


Fig. 4. HCP-pXy-800 @ three electrode set-up in 3 M KOH electrolyte: (a) CVs with different scan rate, (b) CDs with different current density, (c) current density vs specific capacitance, (d) Nyquist plot, (e) cyclic stability test at  $1.25 \text{ A g}^{-1}$  for 2000 cycles and (f) EIS before and after stability test. Inset of (e): SEM images of HCP-pXy-800 electrode after the stability test.

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