Are fractals useful for supercapacitor applications? – A case of Fe_2O_3 negative electrodes

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Materials for supercapacitor applications need high specific surface area to encourage surface charge storage. Hence, several types of morphologies *e.g.* nanoflowers, nanorods, nanofibers *etc*. have been engineered for these applications by various research groups. Most of these materials show promising charge storage performance.

Recently, a different class of morphologies *viz.* 'Fractals' – spatially self-repeating structures – have been explored for supercapacitors. Hota et al. reported that fractals of RuO_2 exhibit the highest areal capacitance of ~11 mF cm^{-2} at 0.1 mA cm^{-2}. We recently demonstrated that fractal-like structures of Fe_2O_3 show a remarkable performance of ~2700 F g^{-1} at 1 A g^{-1}. Inevitably, fractals always have the surface area effects coupled with them. Hence, a morphology with large fractal dimension can possess high specific surface area.

Consequently, some questions are: (i) Are fractals indeed useful for supercapacitor ap-plications? (ii) Can fractality be exploited? (iii) How to decouple surface area effects from fractality? (iv) What are the exclusive effects of the fractal on charge storage mechanism?

These questions are addressed here by studying Fe_2O_3 – a constituent of the commonly available iron oxide – as a negative electrode material. Fe_2O_3 was hydrothermally synthesized in fern, flake and microsphere morphologies with similar specific surface areas (Figure 1a). This was purposefully done to keep the surface area effects the same across these morphologies. The negative electrodes are fabricated by supporting them on nickel foam (NF). The fractal dimensions of these morphologies were estimated geometrically and from electrochemical impedance spectroscopy (FD_{EIS}). The estimated FD_{EIS} for Ferns, Flakes and Microspheres are ~2.50, ~2.36 and ~2.19, respectively. The Fern@NF electrode exhibits the highest specific capacitance (C_{sp}) of ~2708 at 1 A g^{-1}, respectively with a ~94 % capacitance retention after 2000 charge/discharge cycles. Interestingly, the non-Faradaic capacitive surface charge storage from cyclic voltammetry increases with FD_{EIS} from microspheres to ferns. Often, this surface charge storage contribution is modelled using constant phase element (Z_{CPE}) in equivalent electrical circuit (Figure 1b). Our study shows that Z_{CPE} scales inversely with FD_{EIS}. Thus Ferns, with the highest FD_{EIS} exhibit the lowest Z_{CPE}, leading to the highest C_{sp} (Figure 1c).

Hence, fractal-like structures are useful for supercapacitor applications by promoting capacitive surface charge storage through low Z_{CPE}. Fractality of the morphology can be exploited in supercapacitor applications as it is a natural feature in some morphologies of materials which grow freely in nature – *e.g.* iron oxide.
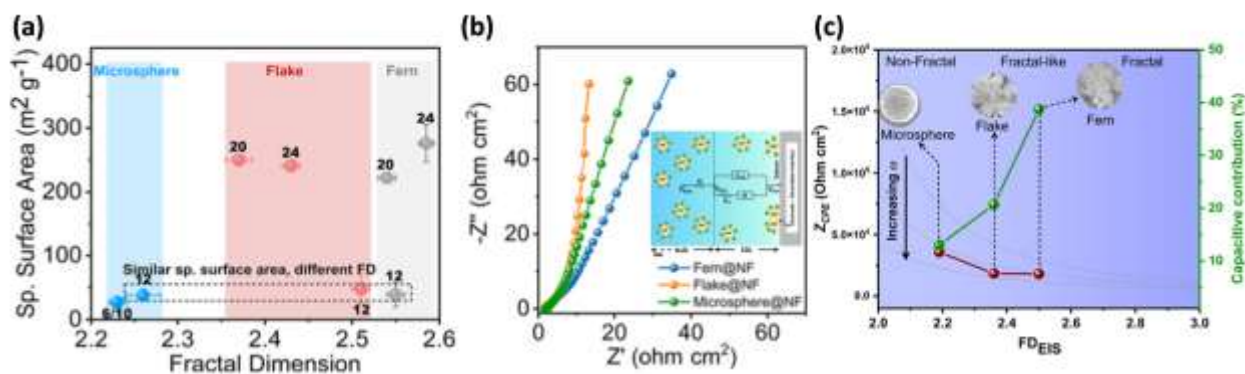

Figure 1. (a) Morphologies with similar specific surface area but different fractal dimensions (the numbers show synthesis duration in hours); (b) Obtained Nyquist plots are modelled using the equivalent circuit shown in the inset; (c) Lower Z_{CPE} leads to higher capacitive contribution in morphologies with larger fractal dimension (FD_{EIS}).

References
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