Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information for "Exploring Non-Linearities of Carbon-Based Microsupercapacitors from an Equivalent Circuit Perspective"

Danupol Boonpakdee, Cristian F. Guajardo Yévenes, Werasak Surareungchai, and Chan La-o-vorakiat*

* chan.lao@kmutt.ac.th

S1. POTENTIAL WINDOW SELECTION

We scanned the voltage over a wide range to find the positive potential where the upturns due to hydrolysis reaction start to be visible (Fig S1). We chose the potential window up to 0.8 V for most of the CV scans presented in the main text. In these measurments, MSCs contain the same LiCl/PVA gel as described in the main text and the scan rate is set to $30\,\mathrm{mV\,s^{-1}}$.

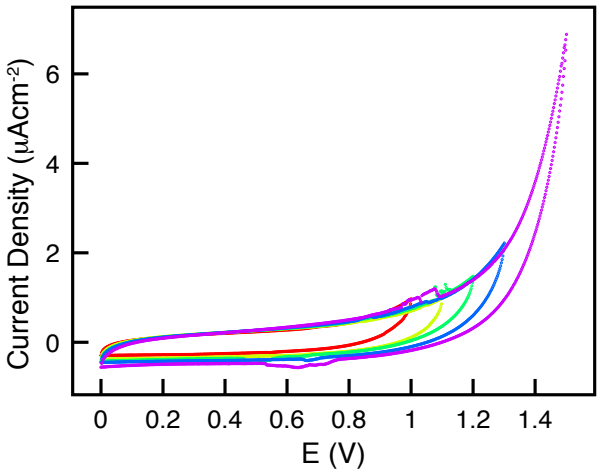


FIG. S1. Selecting the scan potential window to avoid the spike at high potential

S2. SYMMETRIC CV WHEN COMPLETELY SWITCHING THE POLARITY

The CVs are symmetric when the potential sweeps covers both negative and positive potentials symmetrically. Here we have performed the measurements at various scan rates. All could be described by a linear circuit model with three free parameters (C, R_s, R_p). (Fig. S2)

S3. SURVEYING ASYMMETRIC CV IN LITERATURES

To point out that the asymmetric capacitance is not limited to our selection of electrode and electrolyte but rather a general feature in other systems, we extracted 10 CV curves from most cited articles with a keyword "micro-supercapacitor" indexed in Web of Science®

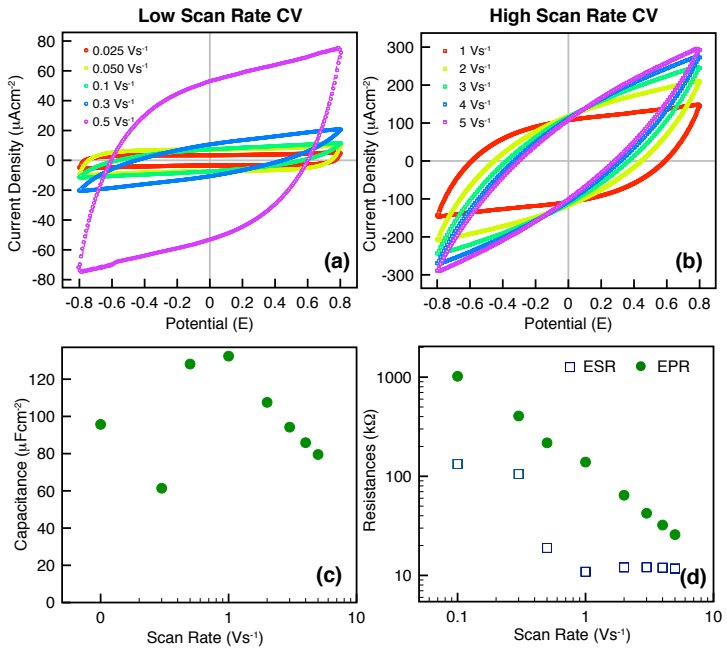


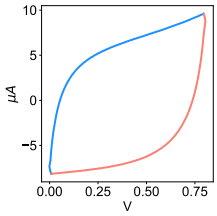
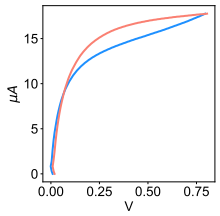
FIG. S2. A completely symmetric CV when reversing the polarity of the electrode for both (a) low and (b) high scan rate to measure (c) capacitance, (d) equivalent serial resistance (circles), and equivalent parallel resistance (open squares). The curve fitting results from a linear equivalent circuit model are displayed as lines.

(only electric double-layer capacitors are included and the results are as of 20 February 2018).

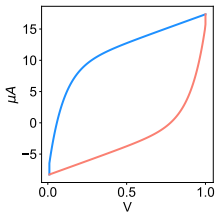
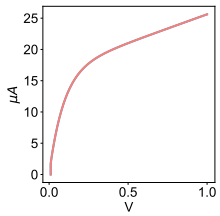
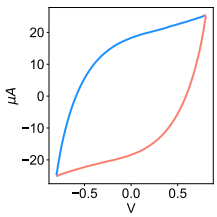
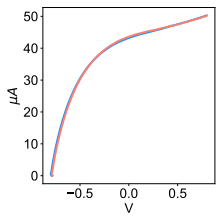
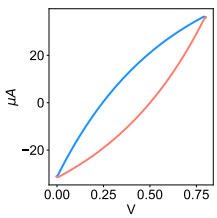
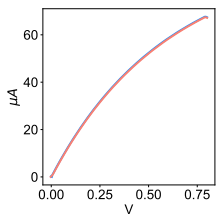
By trying not to over-analyze the data, we simply bisect the CVs into charing (blue) and discharging halves (red); then we invert both current and potential axes of the discharging curve. After offsetting the current level, the two curves should overlap if the circuit parameters are symmetric (as demonstrated by our physical equivalent circuit, simulation and polarity-switched CVs). Our survey gives a surprising result that *all* of the reported CVs process certain degree of asymmetry as in our current work, and most of the curves behave similar to "hidden-storage" non-linearity by having a higher current amplitude of discharging curve.

Using our equivalent circuit approach would deepen the investigation of intricate electrical features of these MSCs beyond the conventional approach.

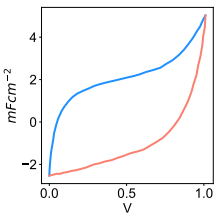
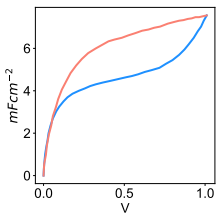
Asymmetric CV from this work

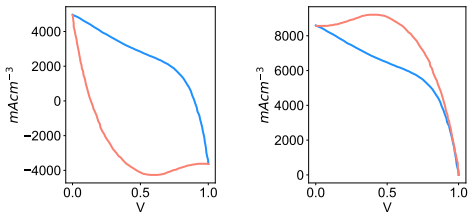
	Original	Inverted	Conditions
1.			main result (Fig. 4c)

Symmetric CVs from this work

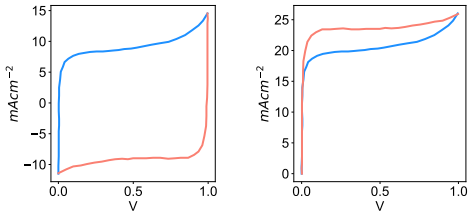
	Original	Inverted	Conditions
1.			equivalent circuit simulation (Fig. 1d)
2.			polarity-switched CV (Fig. 4d)
3.			physical equivalent circuit (Fig. 3b)

CVs from most cited "micro-supercapacitor" articles from Web of Science®

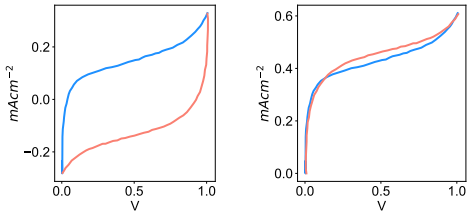
	Original	Inverted	Conditions (electrode/electrolyte, scan rate [ref.])
1.			rGO/GO, 40 mV s^{-1} [1]

2. 

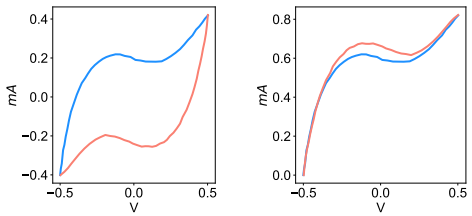
SWNT-rGO fibres/H_3PO_4-PVA, $100\,\mathrm{mV\,s^{-1}}$ [2]

3. 

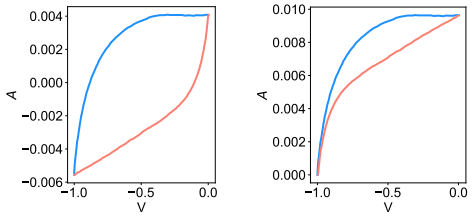
rGO-CNT/KCl, $1\,\mathrm{V\,s^{-1}}$ [3]

4. 

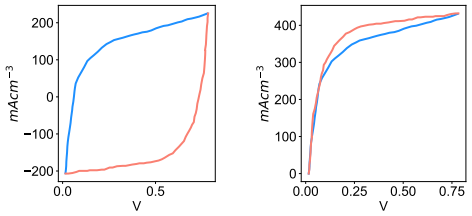
graphene quantum dots/Na_2SO_4, $1\,\mathrm{V\,s^{-1}}$ [4]

5. 

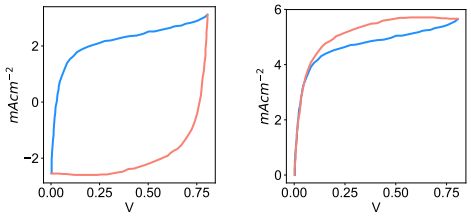
MoS_2, $200\,\mathrm{mV\,s^{-1}}$ [5]

6. 

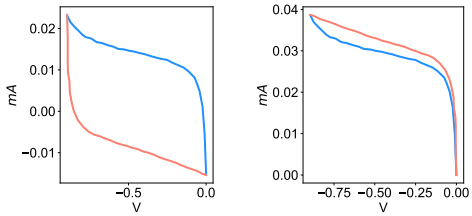
$Ni(OH)_2$ nanowire/KOH-PVA, $200\,\mathrm{mV\,s^{-1}}$ [6]

7. 

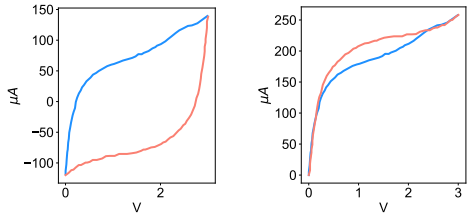
MnO_x−Au/H_2SO_4-PVA, $50\,\mathrm{V\,s^{-1}}$ [7]

8. 

rGO fibers/H_3PO_4-PVA, 20 mV s^{-1} [8]

9. 

rGO-SWCNT fiber/Na_2SO_4-PVP, 10 mV s^{-1} [9]

10. 

SWNT/ionic liquid, 4 V s^{-1} [10]

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[1] Wei Gao, Neelam Singh, Li Song, Zheng Liu, Arava Leela Mohana Reddy, Lijie Ci, Robert Vajtai, Qing Zhang, Bingqing Wei, and Pulickel M. Ajayan. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nat. Nanotechnol.*, 6(8):496–500, 2011.

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[5] Liujun Cao, Shubin Yang, Wei Gao, Zheng Liu, Yongji Gong, Lulu Ma, Gang Shi, Sidong Lei, Yunhuai Zhang, Shengtao Zhang, Robert Vajtai, and Pulickel M. Ajayan. Direct Laser-Patterned Micro-Supercapacitors from Paintable MoS2 Films. *Small*, 9(17):2905–2910, 2013.

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[9] Dingshan Yu, Kunli Goh, Qiang Zhang, Li Wei, Hong Wang, Wenchao Jiang, and Yuan Chen. Controlled Functionalization of Carbonaceous Fibers for Asymmetric Solid-State Micro-Supercapacitors with High Volumetric Energy Density. *Adv. Mater.*, 26(39):6790–6797, 2014.

[10] Daeil Kim, Gunchul Shin, Yu Jin Kang, Woong Kim, and Jeong Sook Ha. Fabrication of a Stretchable Solid-State Micro-Supercapacitor Array. *ACS Nano*, 7(9):7975–7982, 2013.