

Supplementary information for:

**Pentafluoropyridine functionalized novel heteroatom-doped with
hierarchical porous 3D cross-linked graphene for supercapacitor
applications**

Amit Kumar^{1,2}, Chih-Shan Tan², Nagesh Kumar³, Pragya Singh², Yogesh Sharma³,
Jihperng Leu¹, E-Wen Huang¹, Tan Winie⁴, Kung-Hwa Wei¹ and Tseung Yuen Tseng,^{2*}

¹Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu 300, Taiwan.

²Institute of Electronics, National Yang Ming Chiao Tung University, Hsinchu 300, Taiwan.

³Centre of Nanotechnology, I.I.T. Roorkee, Roorkee 247667, India

⁴Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

*Corresponding Author: Tseung Yuen Tseng: E-mail: tseng@nctu.edu.tw;

Tel: +886-3-5731879

Supporting Information;

XRD pattern of graphene oxide (GO) (Fig. S1), Raman spectra of GO (Fig. S2), EDX spectrum of a small physical area and inset shows the elemental composition of the NPF0.3 sample (Fig. S3), HRTEM images of NPF0.3 sample (Fig. S4), Resistance and the electrical conductivity of rGO, PG, NFG, and NPF0.3 samples (Fig. S5), Randles curves and the corresponding diffusion coefficients for rGO and NPF0.3 samples (Fig. S6), CVs of the NPF0.3 electrode (at 25 mVs⁻¹) and the change in specific capacitance as a function of pentafluoropyridine content for as-prepared NPF0.3 electrodes (Fig. S7), CVs of the PG electrode (at 25 mVs⁻¹) and the change in specific capacitance as a function of Phytic acid (PA) content for as-prepared PG electrodes (Fig. S8), Nyquist plot of the device and inset showing the corresponding equivalent circuit diagram after 10000th charge/discharge long cycles (Fig. S9), Brief summary of electrochemical properties of samples (Table S1), Electrochemical performance of the NPF0.3 electrode compared with other recently reported results in the literature (Table S2) are all shown below.

1. XRD analysis of Graphene Oxide (GO)

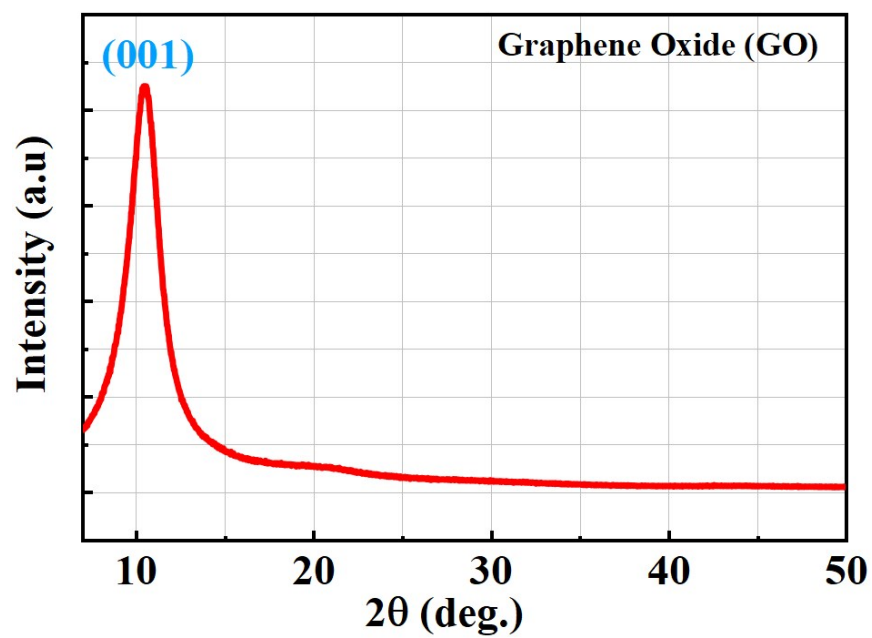


Figure S1. XRD pattern of graphene oxide (GO).

2. Raman analysis of Graphene Oxide (GO)

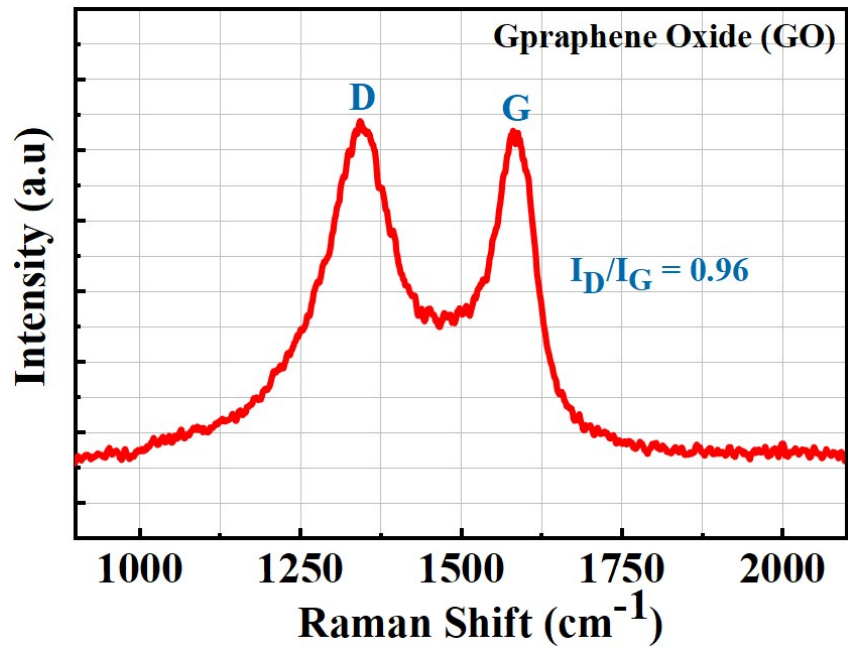


Figure S2. Raman spectra of graphene oxide (GO).

3. EDX spectrum of NCFG-0.3

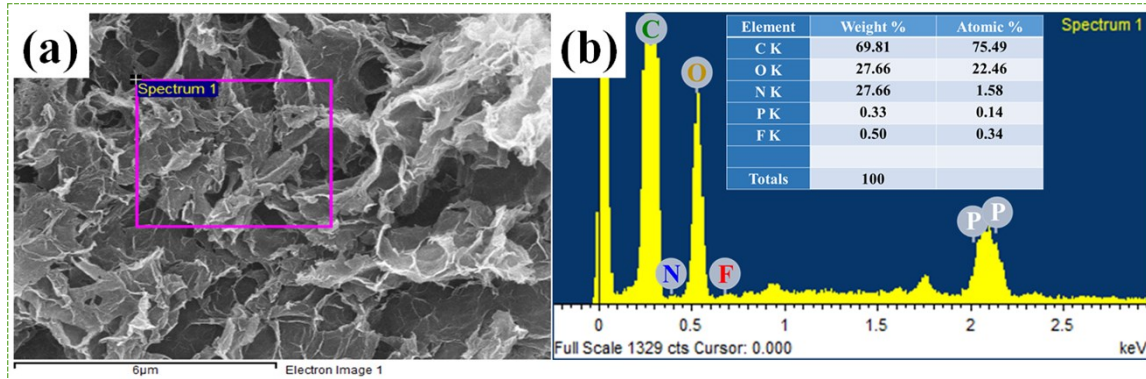


Figure S3. (a) EDX examination of a small physical area and (b) The inset shows the elemental composition of the NCFG-0.3 sample.

4. HRTEM image of NPF0.3

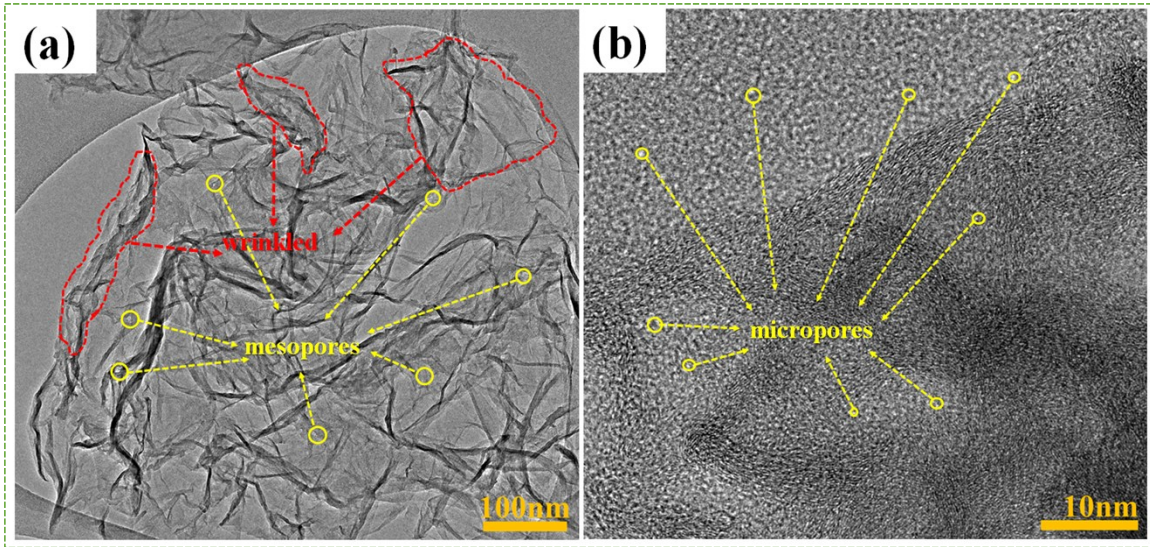


Figure S4. (a-b) HRTEM images of NPF0.3 sample.

5. Electrical conductivity measurements

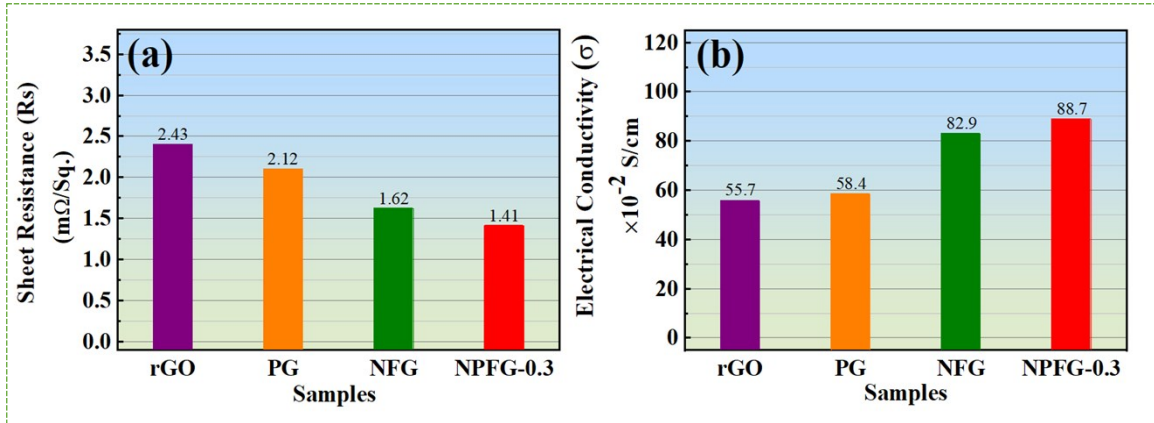


Figure S5. (a) Resistance of rGO, PG, NFG and NPFG-0.3 samples, measured via four probe instruments, and (b) the electrical conductivity of the same.

6. Calculation of Diffusion coefficient (D)

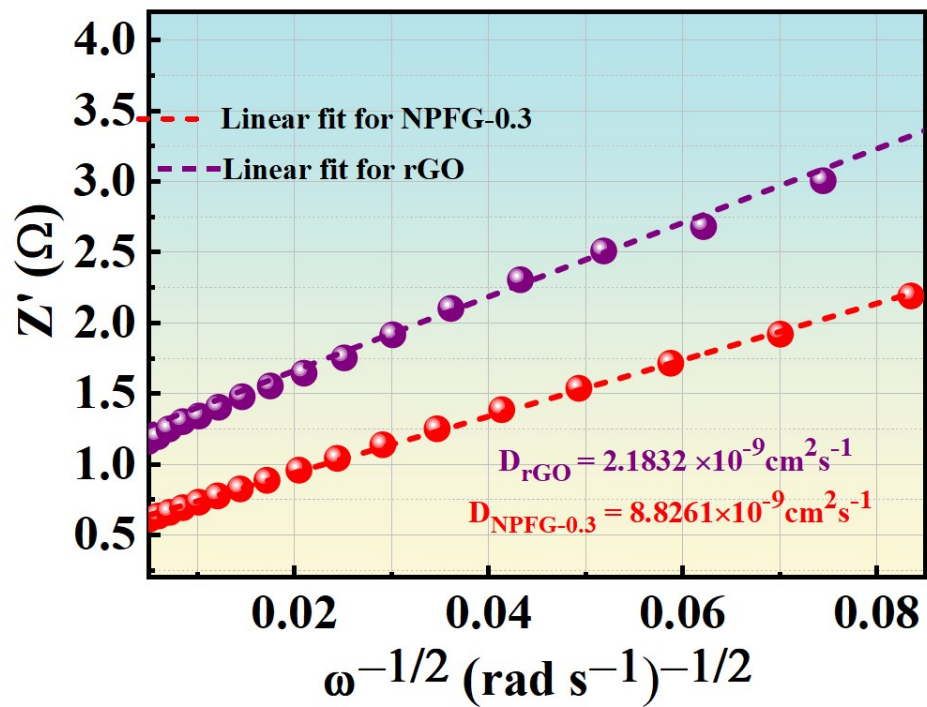


Figure S6. Randles curves and the corresponding diffusion coefficients for rGO and NPGF-0.3 samples.

7. Optimization of the Pentafluoropyridine content

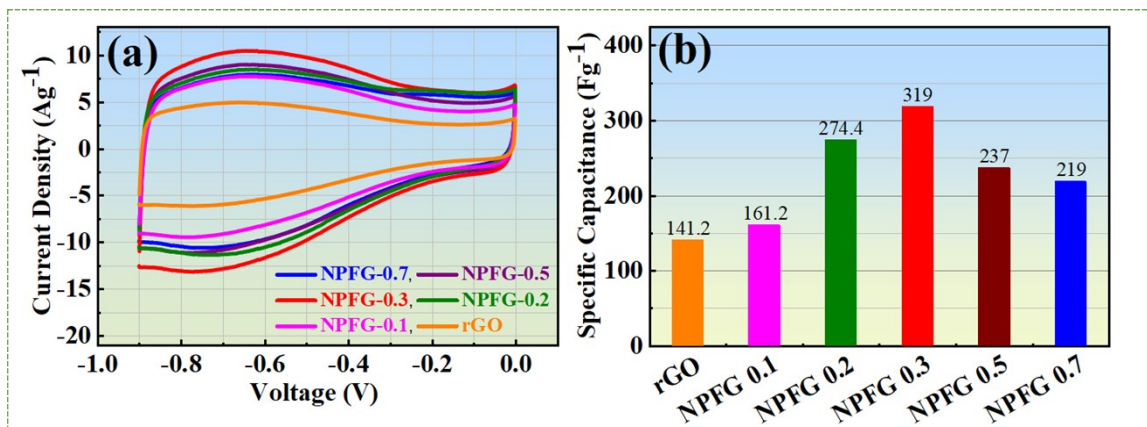


Figure S7. Optimization of pentafluoropyridine content (a) CVs of the NPFGE electrode (at 25 mVs^{-1}) with different pentafluoropyridine content from 0.1 to 0.7 mL, and (b) the change in specific capacitance as a function of pentafluoropyridine content for as-prepared NPFGE electrodes.

8. Optimization of the Phytic acid (PA) content

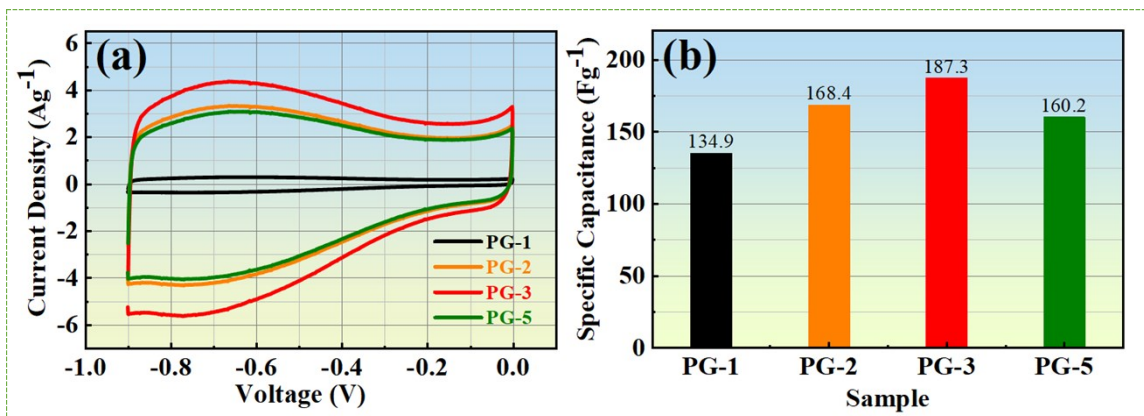


Figure S8. Optimization of Phytic acid (PA) content (a) CVs of the PG electrode (at 25 mVs^{-1}) with different Phytic acid content from 1 to 5 mL, and (b) the change in specific capacitance as a function of Phytic acid (PA) content for as-prepared PG electrodes.

9. Nyquist plot of the device after 10,000th charge/discharge long cycles.

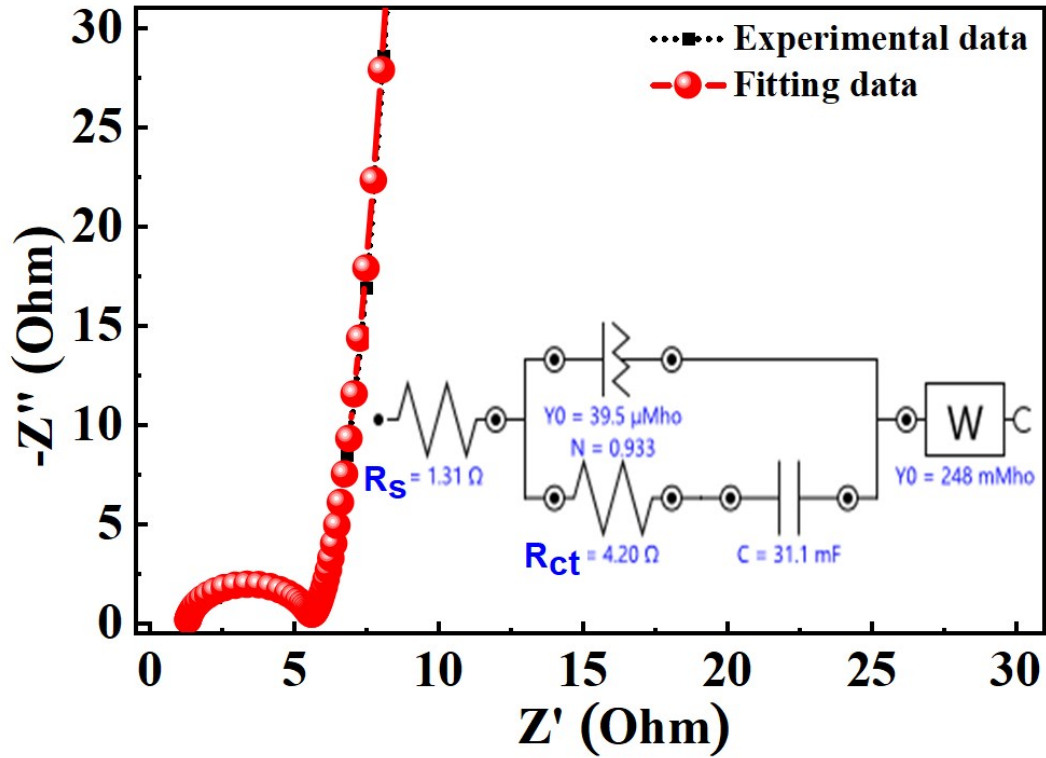


Figure S9. Nyquist plot of the device and inset showing the corresponding equivalent circuit diagram after 10000th charge/discharge long cycles

Table S1 Brief summary of electrochemical properties of the samples.

Sample	Relaxation time constant (τ_0) (ms)	ESR (Rs) (Ω)	Discharge time (s)	Cs (Fg⁻¹) at 0.5 Ag⁻¹
rGO	75.6	0.56	179	161
PG	37.6	0.54	236	170
NFG	40.7	0.5	311	248
NPFG-0.3	28.4	0.47	352	319

Table S2 Electrochemical performance of the NPF0.3 electrode compared with other recently reported results in the literature.

Material	SSA (m²g⁻¹)	Cs (F g⁻¹)	Scan rate/Current density	Electrolyte	Cycle number and retention (%)	Ref.
3D P-doped graphene	637	248.8 Fg ⁻¹	1 Ag ⁻¹	1M H ₂ SO ₄	5000 (89.4%)	[1]
N, P co-doped graphene	284	219.8 Fg ⁻¹	0.25Ag ⁻¹	6M KOH	/	[2]
High-density graphene	/	237 Fg ⁻¹	0.1 Ag ⁻¹	5M KOH	10000 (98%)	[3]
P-graphene	648	239 Fg ⁻¹	1 Ag ⁻¹	6M KOH	5000 (83%)	[4]
3D N-doped graphene	757	175 Fg ⁻¹	0.5 Ag ⁻¹	6M KOH	5000 (87%)	[5]
N, B co-doped graphene	/	217.8 Fg ⁻¹	5 mVs ⁻¹	6M KOH	8800 (103%)	[6]
N, S, P tri-doped graphene	26.7	295	1 Ag ⁻¹	2M KOH	10000 (93%)	[7]
N, S co-doped graphene	252	251 Fg ⁻¹	0.5 Ag ⁻¹	6M KOH	2000 (95%)	[8]
Fluorine-doped graphene	312	279 Fg ⁻¹	0.5 Ag ⁻¹	6M KOH	5000 (94.3%)	[9]
Covalent modified graphene	72.2	287	1 Ag ⁻¹	6M KOH	1000 (94%)	[10]
Phenolic hydroxyl functionalized graphene	321	284.1 Fg ⁻¹	0.3Ag ⁻¹	6M KOH	10000 (88%)	[11]

Alcoholic hydroxyl functionalized graphene	309	260 Fg ⁻¹	0.3Ag ⁻¹	6M KOH	10000 (100%)	[12]
Pentafluoropyridine functionalized 3D graphene (NPPFG-0.3)	518.2	319 Fg ⁻¹	0.5 Ag ⁻¹	6M KOH	15000 (99.8%)	In this work

References

- 1 X.Liu, S.Zou, K.Liu, C.Lv, Z.Wu, Y.Yin, T.Liang and Z.Xie, *J. Power Sources*, 2018, **384**, 214–222.
- 2 K.Xia, Z.Huang, L.Zheng, B.Han, Q.Gao, C.Zhou, H.Wang and J.Wu, *J. Power Sources*, 2017, **365**, 380–388.
- 3 X.Peng, H.Cao, Z.Qin, C.Zheng, M.Zhao, P. Z.Liu, B.Xu, X.Zhou, Z.Liu and J.Guo, *Electrochim. Acta*, 2019, **305**, 56–63.
- 4 L.Wang, H.Tan, J.Chen, H.Zhang, Z.Li and H.Qiu, *Mater. Lett.*, 2019, **252**, 345–348.
- 5 J.Du, L.Liu, Y.Yu, L.Zhang, Y.Zhang and A.Chen, *Mater. Chem. Phys.*, 2019, **223**, 145–151.
- 6 E. C. S. Transactions and T. E. Society, 2018, **85**, 521–530.
- 7 J.Liu, Y.Zhu, X.Chen and W.Yi, *J. Alloys Compd.*, 2020, **815**, 152328.
- 8 J.Li, G.Zhang, C.Fu, L.Deng, R.Sun and C. P. Wong, *J. Power Sources*, 2017, **345**, 146–155.
- 9 T.Jin, J.Chen, C.Wang, Y.Qian and L.Lu, *J. Mater. Sci.*, 2020, **55**, 12103–12113.
- 10 Q.Wang, H.Gao, C.Zhao, H. X. Yue, G.Gao, J.Yu, Y. U.Kwon and Y.Zhao, *Electrochim. Acta*, , DOI:10.1016/j.electacta.2020.137700.
- 11 Y.Zhang, G.Wen, S.Fan, Y.Chu, S.Li, B.Xu and J.Zhang, *J. Power Sources*, 2019, **435**, 226799.
- 12 Y.Zhang, G.Wen, S.Fan, W.Ma, S.Li, T.Wu, Z.Yu and B.Zhao, *Electrochim. Acta*, 2019, **313**, 59–69.