Designing a Graphene Coating-Based Supercapacitor with Lithium Ion Electrolyte: An Experimental and Computational Study via Multiscale Modeling

Joseph Paul Baboo [1], Shumaila Babar [1], Dhaval Kale [1], Constantina Lekakou [1,*] and Giuliano M. Laudone [2]

[1] Centre for Engineering Materials, Department of Mechanical Engineering Sciences, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford GU2 7XH, UK; j.baboo@surrey.ac.uk (J.P.B.); shumaila.babar@surrey.ac.uk (S.B.); dk00197@surrey.ac.uk (D.K.)
[2] Faculty of Science and Engineering, University of Plymouth, Plymouth PL4 8AA, UK; G.Laudone@plymouth.ac.uk
* Correspondence: c.lekakou@surrey.ac.uk

SIMULATION INPUT DATA

Table SI-1. Values of parameters and properties of the electrolyte system used as input data in the continuum simulation in section 4.4

Electrolyte	**1 M $LiPF_6$ /EC:DMC 50:50 v/v**	**Electrolyte**	**1 M $TEABF_4$/ACN**
Solvent viscosity η_o (mPa s)	0.88 [1]	Solvent viscosity η_o (mPa s)	0.34 [6]
Solvent dielectric constant, ε_r	41 taken as average of interpolated values from [2] and [3]	Solvent dielectric constant, ε_r	36 [7]
Desolvated Li^+ d_{Li+} (nm) $d_{Li+,min}$ (nm) $d_{Li+,max}$ (nm) V_{Li+} (nm^3)	 0.18 0.18 0.18 0.00305	Desolvated TEA^+ d_{TEA+} (nm) $d_{TEA+,min}$ (nm) $d_{TEA+,max}$ (nm) V_{TEA+} (nm^3)	 0.706 0.706 1 0.261
Adsorption energy of desolvated Li^+: $\Delta E_{Li+/xGNP\ slit\ pore}$ (kJ mol^{-1})	-99.26	Adsorption energy of desolvated TEA^+: $\Delta E_{TEA+/a\text{-}MWGO\ slit\ pore}$ (kJ mol^{-1})	-48
Desolvated PF_6^- d_{PF6-}(nm) $d_{PF6-,min}$ (nm) $d_{PF6-,max}$ (nm) V_{PF6-} (nm^3)	 0.5 0.5 0.5 0.0654	Desolvated BF_4^- d_{BF4-}(nm) $d_{BF4-,min}$ (nm) $d_{BF4-,max}$ (nm) V_{BF4-} (nm^3)	 0.46 0.46 0.46 0.051
Adsorption energy for desolvated PF_6^-: $\Delta E_{PF6/xGNP\ slit\ pore}$ (kJ mol^{-1})	-28.3	Adsorption energy for desolvated BF_4^-: $\Delta E_{BF4/a\text{-}MWGO\ slit\ pore}$ (kJ mol^{-1})	-19.2
Solvated Li^+/EC:DMC: $d_{Li+/EC:DMC}$ (nm) $d_{Li+/EC:DMC,min}$ (nm) $d_{Li+/EC:DMC,max}$ (nm)	 0.79 0.79 1.16	Solvated TEA^+/ACN $d_{TEA+/ACN}$ (nm) $d_{TEA+/ACN,min}$ (nm) $d_{TEA+/ACN,max}$ (nm)	 1.11 1.11 1.54

$n_{Li+/EC:DMC}$	4	$n_{TEA+/ACN}$	15.5 [8]
$E_{Li+/EC:DMC}$ (kJ/mol)	-65.6	$E_{TEA+/ACN}$ (kJ/mol)	-222 [8]
Desolvation: $\Delta n_{Li+/EC:DMC}$	4	Desolvation: $\Delta n_{TEA+/ACN}$	9.5 [8]
Solvated PF_6/EC:DMC: $d_{PF6-/EC:DMC}$ (nm) $=d_{PF6-/EC:DMC,min}$ $=d_{PF6-/EC:DMC,max}$	0.79 0.79 1.41	Solvated BF_4/ACN: $d_{BF4-/ACN}$ (nm) $=d_{BF4-/ACN,min}$ $=d_{BF4-/ACN,max}$	0.86 0.86 1.45
$n_{PF6-/EC:DMC}$	4	$n_{BF4-/ACN}$	6.75 [8]
$E_{PF6-/EC:DMC}$ (kJ/mol)	-6.7	$E_{BF4-/ACN}$ (kJ/mol)	-196 [8]
$\Delta n_{PF6-/EC:DMC}$	4	$\Delta n_{BF4-/ACN}$	3.4 [8]
Conductivity σ_2 (S m^{-1})	1.14 [4-5]	Conductivity σ_2 (S m^{-1})	6 [9]

Table SI-2. Input data for the electrodes xGNP-750 and a-MWGO [10] for the continuum simulations in section 4.4

Table SI-2a. Input data for the electrode xGNP-750; coating thickness = 60 μm; coating areal density = 1.10 mg cm^{-2} (from the experimental part of this study)

No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
d_p (nm)	$15x10^3$	144.66	87.23	50.32	32.16	19.52	12.83	9.93
ΔV_p (cm^3 g^{-1})	2.127	0.03055	0.05415	0.0857	0.1815	0.0891	0.0892	0.1476
No	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
d_p (nm)	6.89	3.46	1.97	1.61	1.41	1.31	0.635	0.5725
ΔV_p (cm^3 g^{-1})	0.1125	0.059951	0.018438	0.0142	0.00913	0.01887	0.00515	0.007267
No	**17**							
d_p (nm)	0.3788							
ΔV_p (cm^3 g^{-1})	0.00054							

Table SI-2b. Input data for the electrode a-MWGO, derived from the processing and discretisation of the PSD in [10]; coating thickness = 60 μm; coating areal density = 1.25 mg cm^{-2} [10]

No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
d_p (nm)	500	39.99	33.44	24.45	12.6	10.9	9.46	8.65
ΔV_p (cm^3 g^{-1})	13.21	0.01018	0.0045	0.0032	0.0038	0.003	0.0045	0.0056
No	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
d_p (nm)	8.2	7.65	7.07	6.84	6.39	6.11	5.85	5.72
ΔV_p (cm^3 g^{-1})	0.0072	0.0099	0.0125	0.015	0.022	0.024	0.028	0.032
No	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
d_p (nm)	5.47	5.35	5.17	4.835	4.73	4.68	4.42	4.135
ΔV_p (cm^3 g^{-1})	0.0362	0.041	0.0434	0.0449	0.0478	0.051	0.055	0.0555
No	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**
d_p (nm)	3.95	3.82	3.7	3.58	3.5	3.3	3.2	3.13
ΔV_p (cm^3 g^{-1})	0.1164	0.1130	0.1040	0.0938	0.0818	0.0688	0.0582	0.0439
No	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
d_p (nm)	2.89	2.86	2.64	2.45	2.34	2.16	2.04	1.96
ΔV_p (cm^3 g^{-1})	0.0375	0.0395	0.0387	0.0341	0.0304	0.0265	0.0227	0.024
No	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**
d_p (nm)	1.89	1.77	1.73	1.55	1.54	1.5	1.45	1.38
ΔV_p (cm^3 g^{-1})	0.0247	0.0248	0.0255	0.0243	0.0233	0.0265	0.0235	0.0215
No	**49**	**50**	**51**	**52**	**53**	**54**	**55**	**56**
d_p (nm)	1.32	1.28	1.24	1.18	1.11	1.07	1.01	0.99
ΔV_p (cm^3 g^{-1})	0.0189	0.0154	0.011	0.0086	0.0055	0.0062	0.0069	0.0078
No	**57**	**58**	**59**	**60**	**61**	**62**	**63**	**64**
d_p (nm)	0.98	0.935	0.89	0.855	0.82	0.78	0.75	0.72
ΔV_p (cm^3 g^{-1})	0.0089	0.0105	0.0152	0.0151	0.0158	0.0132	0.01289	0.0103
No	**65**	**66**	**67**	**68**	**69**	**70**	**71**	**72**
d_p (nm)	0.67	0.65	0.64	0.60	0.57	0.55	0.52	0.50
ΔV_p (cm^3 g^{-1})	0.0108	0.0111	0.0147	0.0171	0.0152	0.0136	0.0125	0.0099
No	**73**	**74**	**75**	**76**	**77**			
d_p (nm)	0.48	0.46	0.44	0.42	0.40			
ΔV_p (cm^3 g^{-1})	0.0065	0.0042	0.0030	0.00135	0.0007			

REFERENCES

[1] M. Dahbi, F. Ghamouss, F. Tran-Van, D. Lemordant, M. Anouti, Comparative study of EC/DMC LiTFSI and LiPF6 electrolytes for electrochemical storage. Journal of Power Sources 196 (2011) 9743– 9750.

[2] I.N. Daniels, Z. Wang, B.B. Laird, Dielectric properties of organic solvents in an electric field. J. Phys. Chem. C 121 (2017) 1025–1031.

[3] E.R. Logan, E.M. Tonita, K. L.Gering, L. Ma, M.K.G. Bauer, J. Li, L.Y. Beaulieu, J.R. Dahn, A study of the transport properties of ethylene carbonate-free Li electrolytes. Journal of The Electrochemical Society 165 (2018) A705-A716.

[4] C.L. Berhaut, D. Lemordant, P. Porion, L. Timperman, G.Schmidt, M. Anouti, Ionic association analysis of LiTDI, LiFSI and $LiPF_6$ in EC/DMC for better Li-ion battery performances. RSC Adv. 9 (2019) 4599–4608.

[5] "Electrolytes for lithium and lithium-ion batteries" ed. T.R. Jow, K. Xu, O.Borodin, M. Ue, 2014, Springer, New York, p.384

[6] V. N. Afanas'ev, E.Y. Tyunina, M. D. Chekunova, The influence of temperature and concentration on viscous flow of solutions of Et_4NBF_4 in propylene carbonate. Russian Journal of Physical Chemistry A 83 (2009) 2069–2073.

[7] Z. Zhang, Y. Lai, J, Li , Y. Liu, Electrochemical behavior of wound supercapacitors with propylene carbonate and acetonitrile based nonaqueous electrolytes, Journal of Central South University of Technology 16 (2009) 247-252.

[8] G. Feng, J. Huang, B.G. Sumpter, V. Meunier , R. Qiao, Structure and dynamics of electrical double layers in organic electrolytes, Phys. Chem. Chem. Phys. 12 (2010) 5468–5479.

[9] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Desolvation of ions in subnanometer pores and its effect on capacitance and double-layer theory, Angew. Chem. Int. Ed. 47 (2008) 3392 –3399.

[10] Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, D. Su, E.A. Stach, R.S. Ruoff, Carbon-based supercapacitors produced by activation of graphene. Science 332 (2011) 1537–1541.