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More sustainable energy storage: lignin based electrodes with glyoxal crosslinking

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Supporting Information

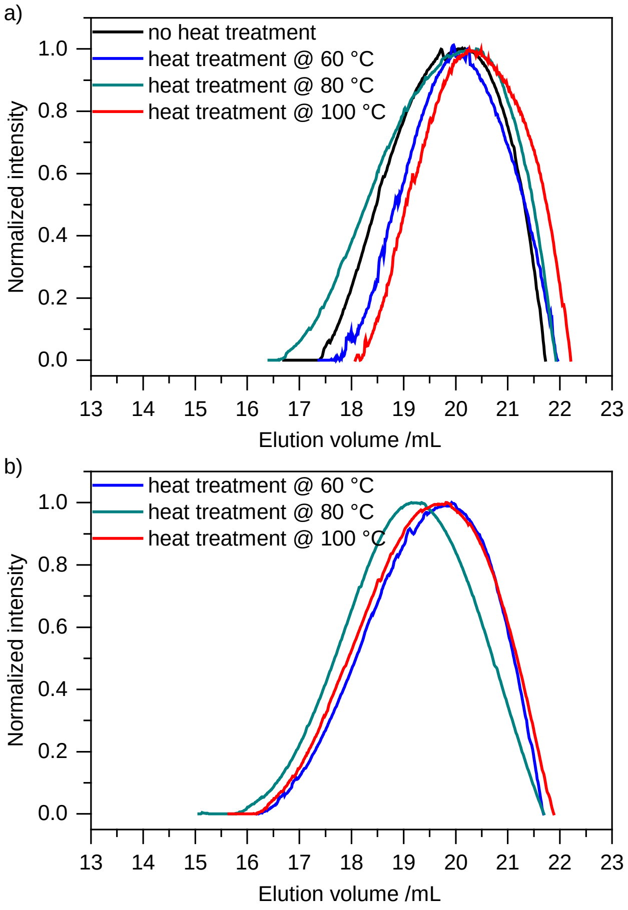

Figure ESI-1: GPC traces in NMP of samples that were heat treated at different temperature as indicated. a) Neat lignin; b) lignin in the presence of glyoxal.

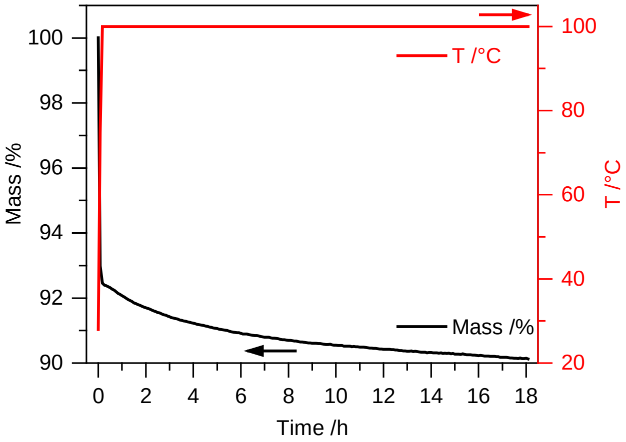

Figure ESI-2: Thermogravimetric analysis of lignin during heating to 100 °C and holding at this temperature for 18 h.

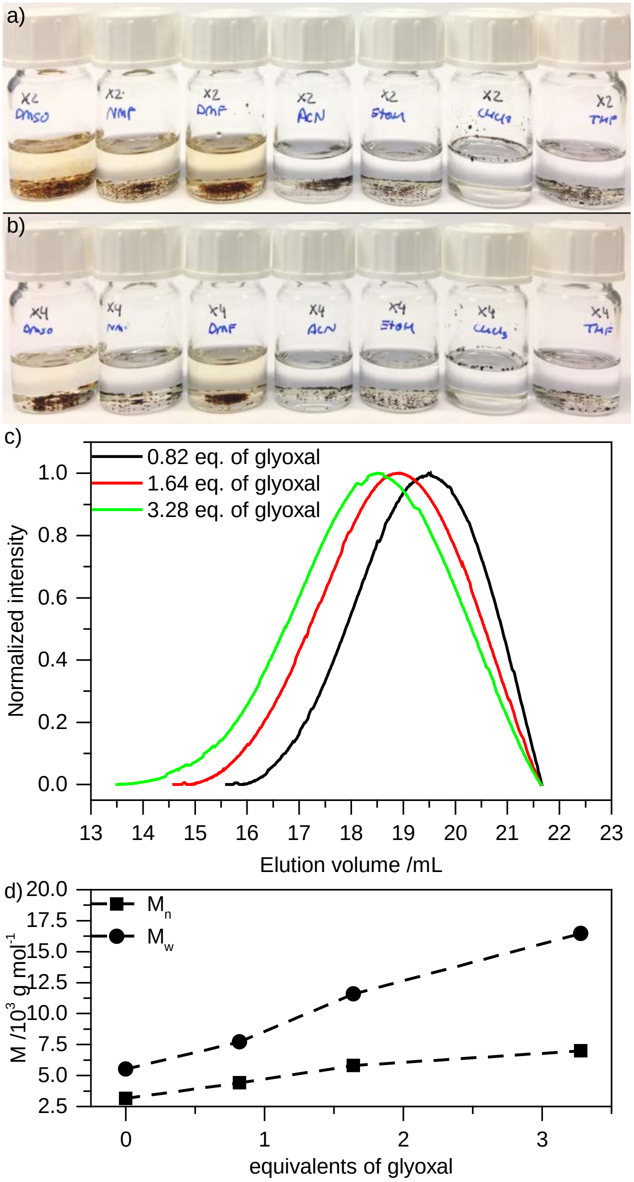

Figure ESI-3: a,b) Photographs of solutions (1 mg mL^{-1}) of lignin which was treated with glyoxal at elevated temperature of 60 °C for 18 h and subsequently at 80 °C for 2 h (from left to right: solution in DMSO, NMP, DMF, ACN, ethanol, chloroform, and THF). The amount of glyoxal was two times (a; 1.64 eq. of glyoxal) or four times (b; 3.28 eq. of glyoxal) as high as in Error! Reference source not found.. **c) GPC traces in NMP of these samples and the sample with the original glyoxal:lignin ratio (soluble fraction). d) Molecular weight as determined from (c).**

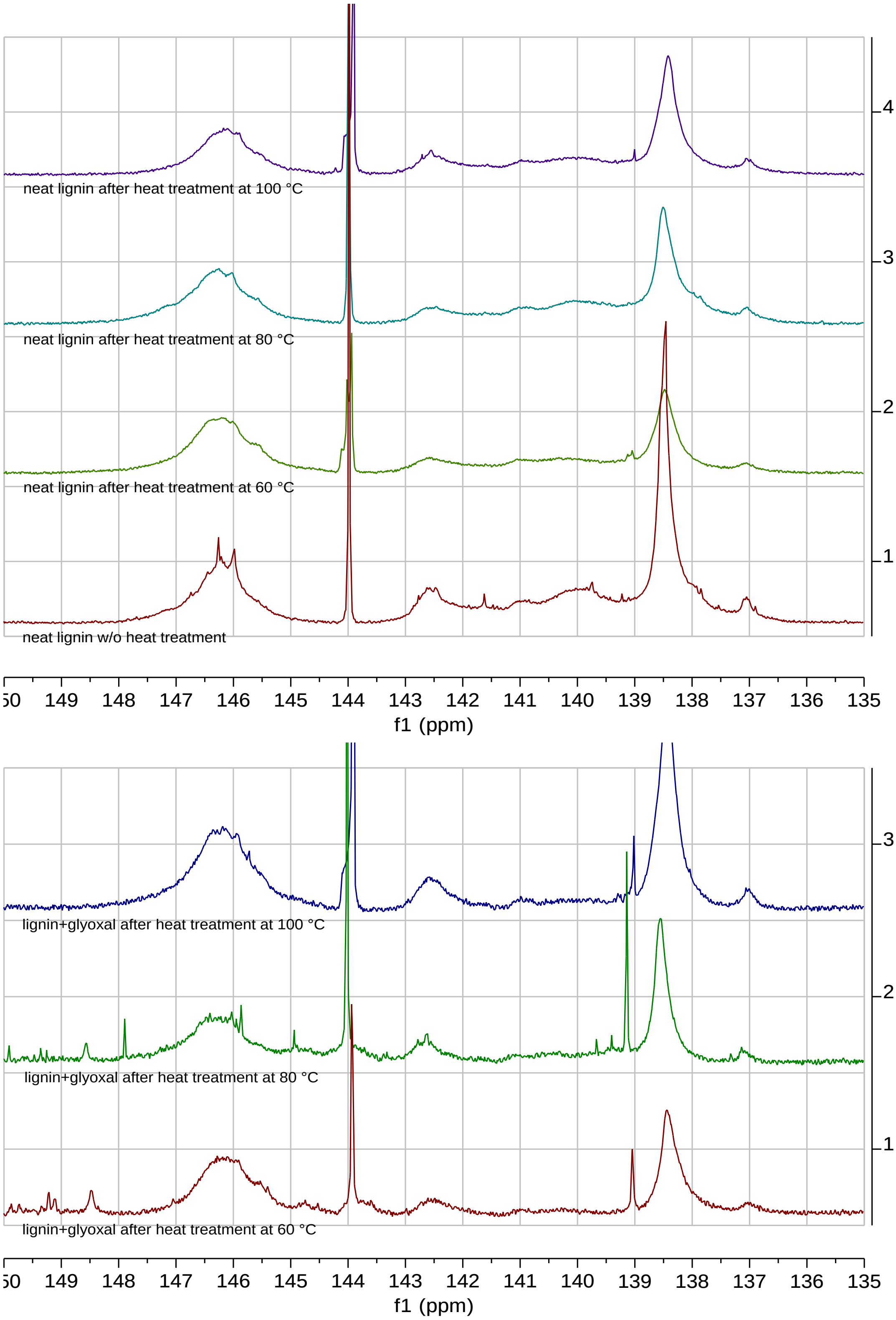

Figure ESI-4: ^{31}P NMR spectra of the original lignin as well as heat treated and glyoxalated lignin after phosphitylation.

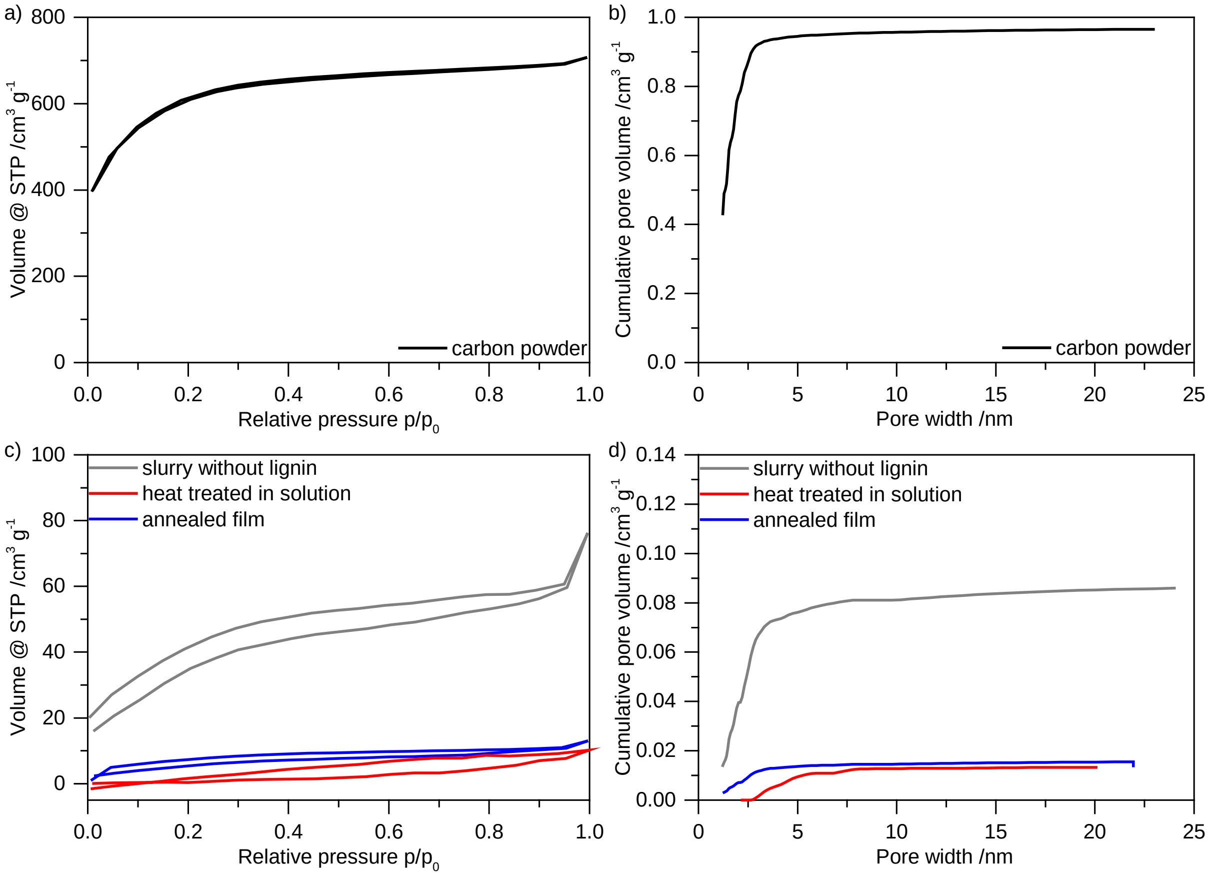

Figure ESI-5: a,c) N_2 sorption measurements (volume at standard temperature and pressure as a function of the relative pressure) of high surface area active carbon powder (a) or glyoxalated lignin based electrodes with high surface area active carbon after processing in NMP (blue, red) or comparable electrodes from high surface area active carbon (gray) (c). b) and d) show the cumulative pore volume as calculated from BET isotherms of the sorption measurements a) and c), respectively.

Table ESI-1: Pore composition of the samples investigated by N_2 sorption experiments in Figure ESI-5 as determined from BET isotherms.

sample	micropore volume /cm^3 g^{-1}	mesopore volume /cm^3 g^{-1}	total pore volume /cm^3 g^{-1}	S_{BET} /m^2 g^{-1}
carbon powder	$9.85 \cdot 10^{-1}$	$1.10 \cdot 10^{-1}$	1.094	2141
slurry without lignin	$6.29 \cdot 10^{-2}$	$5.51 \cdot 10^{-2}$	$1.18 \cdot 10^{-1}$	135
heat treated in solution	$1.69 \cdot 10^{-3}$	$1.41 \cdot 10^{-2}$	$1.58 \cdot 10^{-2}$	2
annealed film	$1.00 \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$	22

The hysteresis of the isotherms in Figure ESI-5c indicates that there is some small molecule in the pores. This especially leads to drastically reduced micropore volume but also significantly decreasing mesopore volume (comparison of the black and gray curves in Figure ESI-5; first and second line in Table SI-). Samples with lignin (blue and red curves in Figure ESI-5; third and fourth line in Table SI-) contain only 50% carbon. If lignin (and glyoxal) does not contribute to the pore volume, the surface area of the film in which lignin was crosslinked during annealing is approx. one third of the pure carbon while the surface area of the film in which lignin was crosslinked before film formation is still negligible. Note that numbers below 100 m^2 g^{-1} are prone to very high errors.

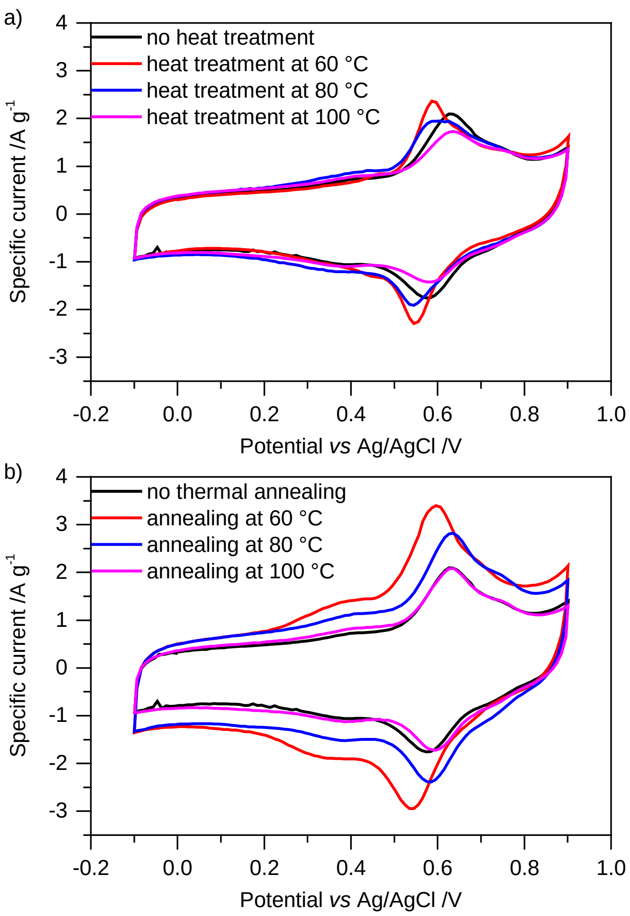

Figure ESI-6: Cyclic voltammetry scans of of glyoxalated lignin based electrodes (with high surface area active carbon).a) Lignin was glyoxalated in solution at the indicated temperature for 18 h before electrode slurry formation; b) a slurry of lignin, glyoxal, and high surface area active carbon was annealed at the indicated temperature for 18 h.

Table ESI-2: Electrode mass after annealing at elevated temperature and after subsequent drying in vacuum at room temperature in order to remove traces or remaining solvent.

composition	m(substrate) /g	m(coated substrate before annealing) /g	m(w/o solvent and substrate) /mg	m(coated substrate after 18 h) /g	Δm(after 18 h) /mg	m(coated substrate after 7 days) /g	Δm(after 7 days) /mg	m(coated substrate after 14 days) /g	Δm(after 14 days) /mg
lignin + carbon	0.10136	0.27455	31.34	0.13910	37.74	0.13360	32.24	0.13345	32.09
	0.10200	0.27950	32.12	0.14150	39.50	0.13606	34.06	0.13585	33.85
	0.10166	0.27890	32.07	0.14050	38.84	0.13460	32.94	0.13441	32.75
average			31.84		38.69		33.08		32.90
lignin + carbon + glyoxal	0.10225	0.28300	33.52	0.14338	41.13	0.13855	36.30	0.13815	35.90
	0.10236	0.28198	33.31	0.14348	41.12	0.13921	36.85	0.13879	36.43
	0.10123	0.27436	32.11	0.14188	40.65	0.13535	34.12	0.13529	34.06
average			32.98		40.97		35.76		35.46

The gravimetric determination shows that after 18 h at elevated temperature in vacuum, there is still a low amount of NMP in the electrode material. Even after two weeks in vacuum at room temperature, there is approx. 1.06 mg NMP in test samples of 31.84 mg lignin + high surface area active carbon. Samples which additionally contain glyoxal are in average 2.48 mg heavier after annealing for 2 weeks in vacuum than after film formation. This indicates that glyoxal, despite the low boiling point of approx. 50 °C, did not evaporate during annealing in vacuum at elevated temperature and also did not stay in the film in unbound form (films would be lighter than before drying due to evaporating glyoxal) but reacts with lignin during annealing or even during slurry formation by mortar and pestle.

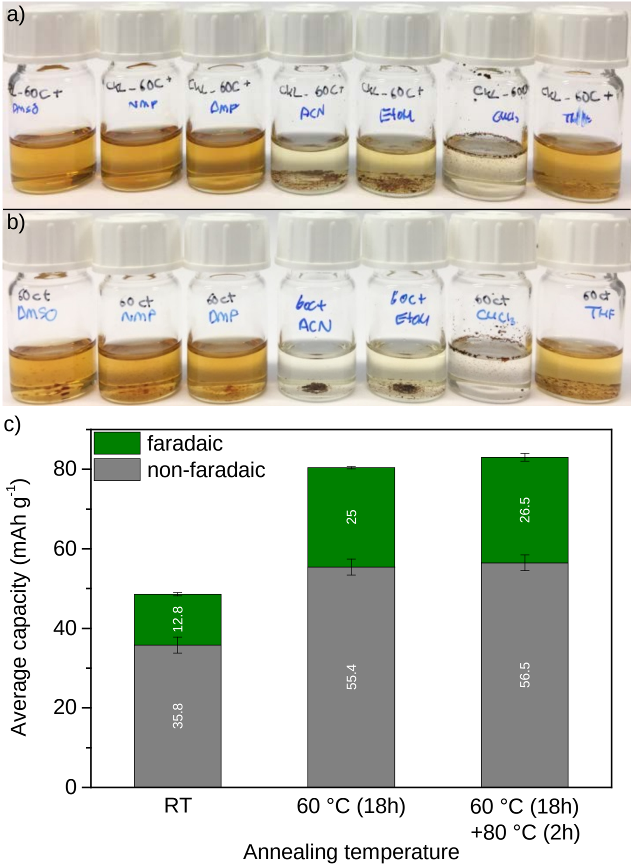

Figure ESI-7: (a,b) Photographs of solutions (1 mg mL^{-1}) of lignin which was treated without (a) or with (b) glyoxal at elevated temperature of 60 °C for 18 h and subsequently at 80 °C for 2 h (from left to right: solution in DMSO, NMP, DMF, ACN, ethanol, chloroform, and THF). (c) Capacity of glyoxalated lignin based electrodes (with high surface active carbon) in dependence of the temperature at which the electrodes were annealed.

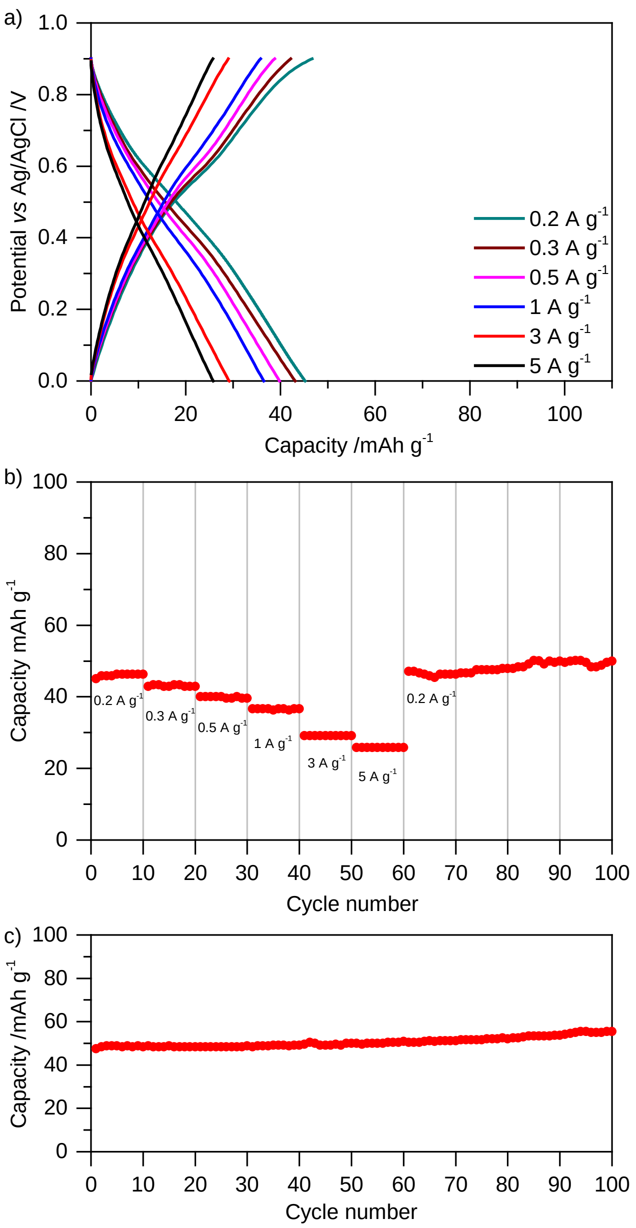

Figure ESI-8: Electrochemical behavior of glyoxalated lignin based electrodes, in which lignin was heat treated with glyoxal at 60 °C for 18 h and subsequently at 80 °C for 2 h before electrode formation. (a) Galvanostatic charge-discharge measurements and (b) rate performance at different current densities as denoted in the figures. (c) Cycling stability at a current density of 0.2 A g^{-1}.

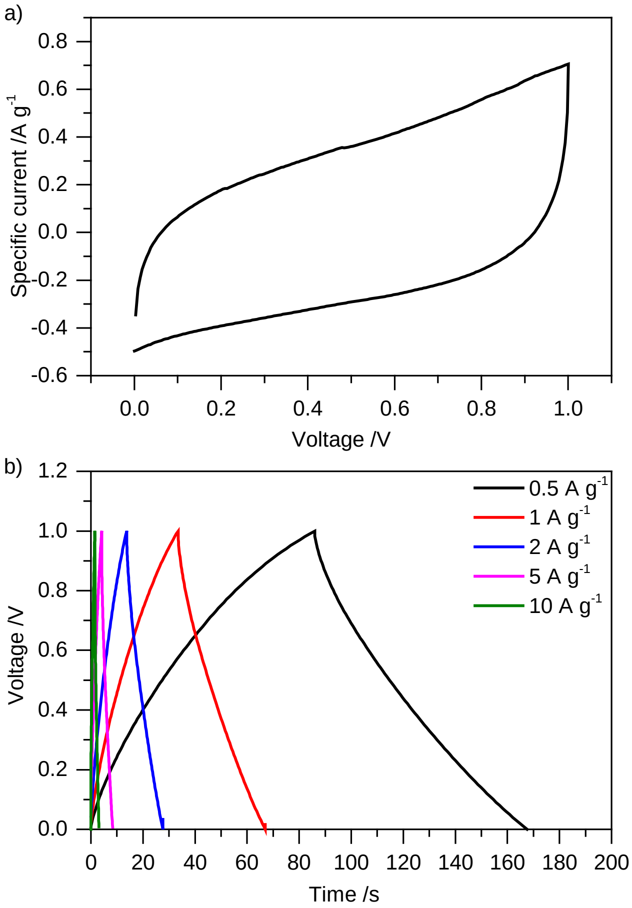

Figure ESI-9: Cyclic voltammetry (a) and galvanostatic charge-discharge measurements of a symmetrical 2-electrode cell using glyoxalated lignin based electrodes.