Supplemental Information

Anthraquinone-2,6-disulfamidic acid: An anolyte with low decomposition rates at elevated temperatures

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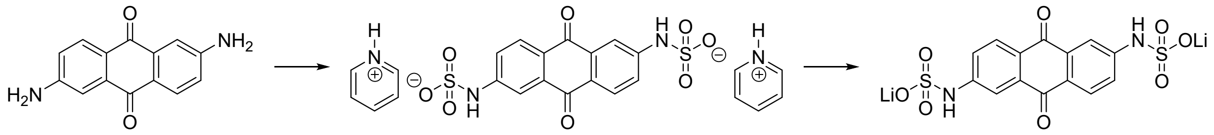
General analytical instruments

The NMR spectra were obtained utilizing an Advance I 300 MHz (Bruker, Germany) or an Avance III 400 MHz (Bruker, Germany). The ESI-Q-TOF MS measurements were performed applying a micrOTOF QII mass spectrometer (Bruker, Germany) with an automatic syringe pump (KD Scientific, USA). An ESI source was used to generate ions and the calibrated instrument measured in a m/z range between 50 and 3000. As calibration standard, an ESI-L Low concentration tuning mix from Agilent was utilized. The sample concentration ranged between 1 and 10 μg mL^{-1}. The samples were injected in the instrument with a constant flow of 3 μL min^{-1} (= 180 μL hr^{-1}). The data were evaluated with the Bruker Data Analysis software version 4.2. For pH-measurements, a Mettler Toledo FiveGO F2 equipped with a Mettler Toledo LF438 pH-electrode was used. For the FT-IR spectroscopy investigations an Invenio S (Bruker, Germany) with a Platinum ATR (Bruker, Germany) was used.

Chemicals and materials

If not noted otherwise, the solvents were purchased from standard suppliers and distilled prior to usage. If solvents were used from a solvent purification system (SPS), they were obtained from an MB-SPS-800 (MBraun Inertgas-Systeme GmbH, Germany) and stored under argon. If water was used, deionized water was utilized. 2,6-Diaminoanthraquinone (Sigma-Aldrich, Germany), lithium chloride (Sigma-Aldrich, Germany), pyridine (Fisher Scientific, Germany), chlorosulfuric acid (Merk, Germany), potassium ferrocyanide trihydrate (Sigma-Aldrich, Germany) were purchased by the corresponding suppliers and used as received.

Synthesis of lithium anthraquinone 2,6-bis(sulfamate)



30 g (126 mmol) of 2,6-diaminoanthraquinone was suspended in 600 mL of dichloromethane in a 1.5 L sulfonation flask equipped with a KPG (sealed precision glass) stirrer, a reflux condenser, dropping funnel and a thermometer. The mixture was cooled to 0 °C in an ice bath. 27.2 mL (44.04 g, 378 mmol) chlorosulfuric acid diluted with 60 mL dichloromethane was added to the mixture. During the addition, the suspension turned from brown-red to green-grey. Afterwards the reaction mixture was stirred for 30 min and, subsequently, 47.7 mL pyridine diluted with 60 mL dichloromethane was added slowly dropwise. The temperature of the mixture increased during the addition and the mixture turned to light brown. After complete addition, the mixture was allowed to heat to room temperature, was stirred for 16 h, and then stirred under reflux conditions for additional 2 h. After cooling to room temperature, the formed participate was collected by filtration and washed with dichloromethane and acetone. The solid was added to 1.5 L of water, but did not completely dissolve. Lithium hydroxide was added until the pH value of the solution reached 12. The solid dissolved upon basification nearly completely and the mixture turned from light brown to dark red. Remaining solid was removed by filtration. The filtrate was concentrated by removing the solvent. The mixture was then added dropwise to 1.5 L of acetone and the precipitate was collected by filtration. The solid was washed with acetone to receive the desired product as red-brownish solid (42.2 g, 103 mmol, 82%) ^{1}H NMR (D$_2$O, 300 MHz): δ [ppm] = 7.09 (2 H, m, C-C*H*-CNH), 7.18 (2 H, d, J = 2.26 Hz, CH-C*H*-CNH), 7.51 (2 H, m, d, J = 8.48 Hz, C*H*-CH-CNH), ^{13}C NMR (D$_2$O, 75 MHz): δ [ppm] = 113.65 (C$_{1+5}$), 120.98 (C$_{3+7}$), 124.92 (C$_{12+14}$), 129.02 (C$_{8+4}$), 134.02 (C$_{13+11}$), 147.57 (C$_{2+6}$), 182.75 (C$_{9+10}$), (the additional peak at 168.06 ppm corresponds

to the C_9 and C_{10} and is caused by tautomerism)[1, 2]. ^{7}Li NMR (D_2O, 155 MHz): δ [ppm] = 0.02 (s), HR-MS (ESI m/z): calc. for $[C_{14}H_8N_2O_8S_2]^{2-}$ 197.9867 found 197.9856.

Solubility measurement

An excess amount of 2.6-diamino anthraquinone (DAAQ) was placed into 1.5 mL pure water or electrolyte (0.25 M LiOH and 1 M LiCl). After vortexing it for 6 hours the suspension was filtered with a syringe filter (0.45 µm, Nylon 66, Applichrom, Germany) and adequate amounts of solution were transferred into a HPLC vial and freeze dried. The solubility of the compound was calculated by the mass differences with taking the electrolyte salt into account. The same was done for the LiAQS in pure water.

Table 1: Maximum solubility of DAAQ and LiAQS.

Compound	Solvent	Maximum concentration
DAAQ	pure water	0.051 M
DAAQ	electrolyte	0.081 M
LiAQS	pure water	0.373 M
LiAQS	electrolyte	0.750 M

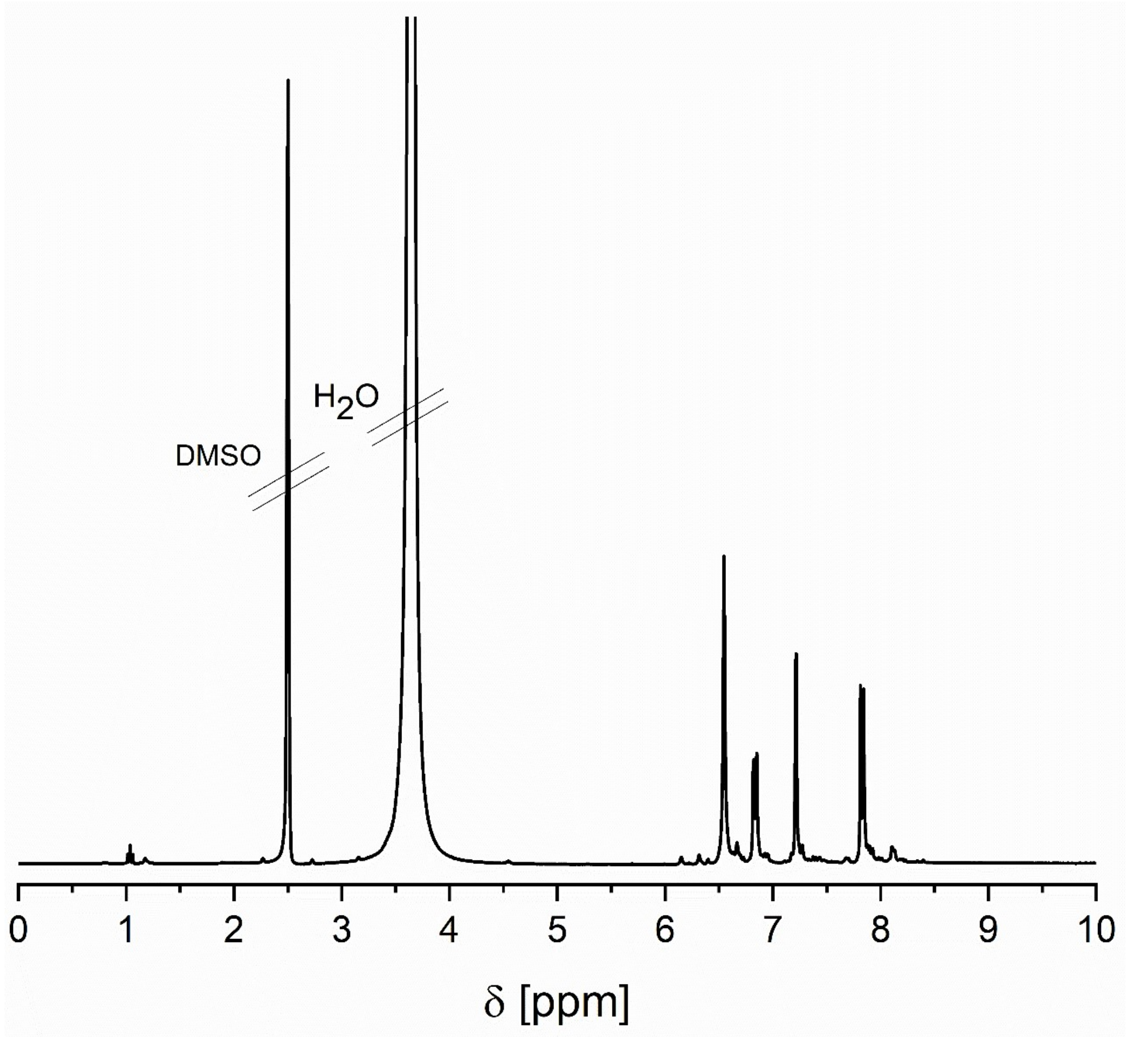


Figure 1: ^{1}H NMR spectrum of 2,6-diaminoanthraqinone (Sigma Aldrich) (300 MHz, DMSO-d_6).

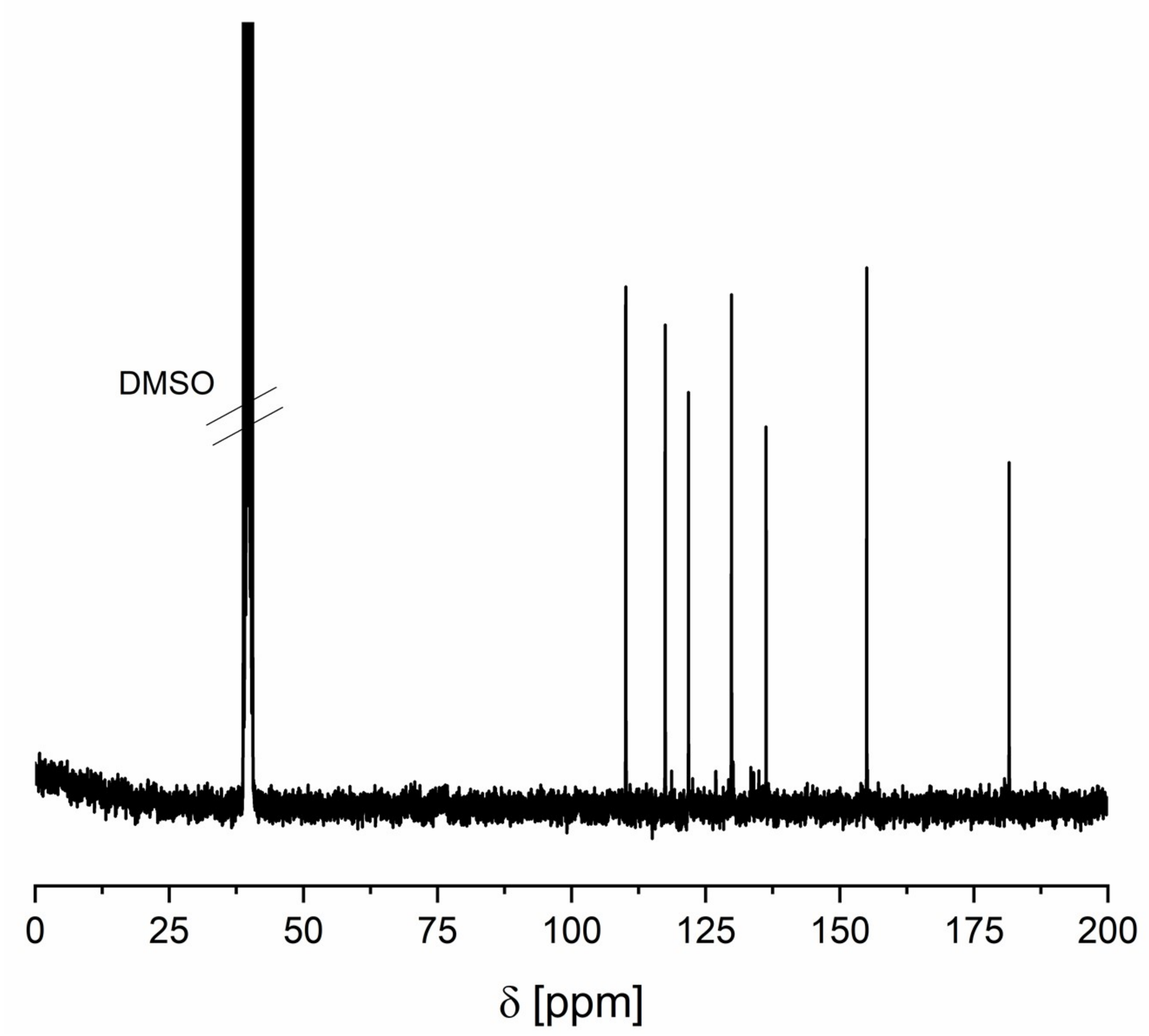


Figure 2: ^{13}C NMR spectrum of 2,6-diaminoanthraquinone (Sigma Aldrich) (300 MHz, DMSO-d_6).

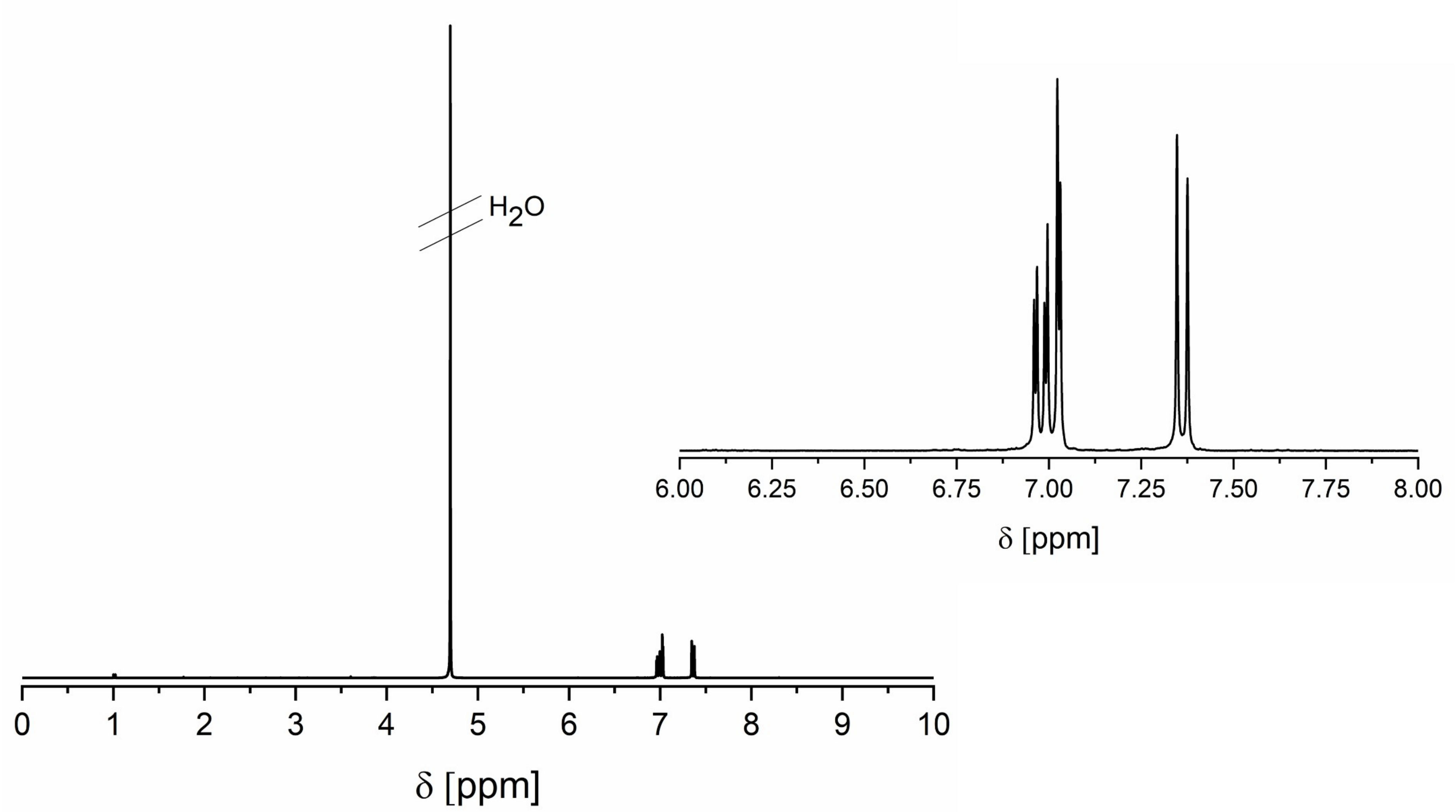
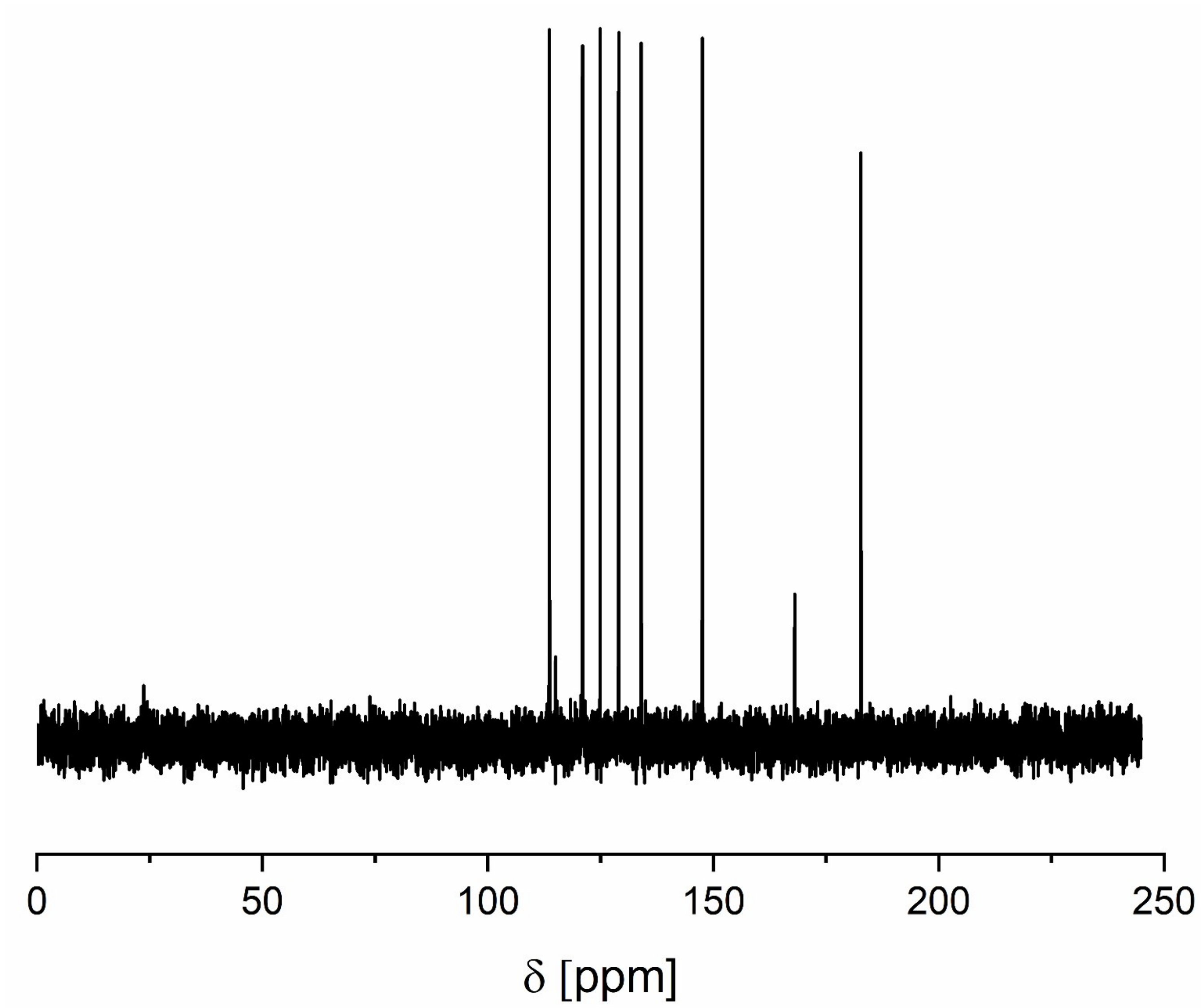


Figure 3: ^1H NMR spectrum of lithium anthraquinone 2,6-bis(sulfamate) (300 MHz, deuterated water). Inlet shows the zoomed spectrum between 6.00 and 8.00 ppm.



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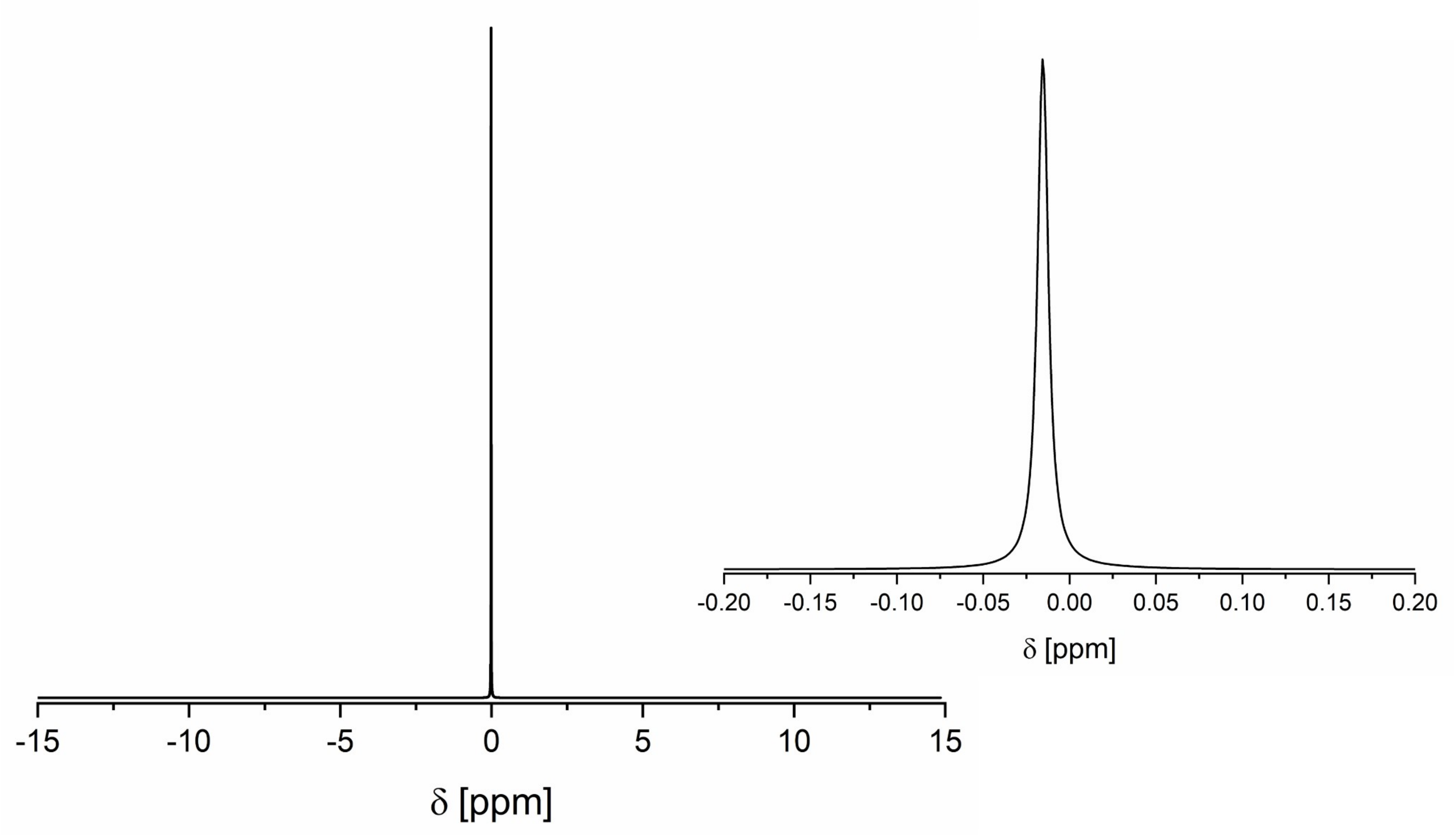
84 *Figure 4: ^{13}C NMR spectrum of lithium anthraquinone 2,6-bis(sulfamate) (75 MHz, deuterated water).*



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86 *Figure 5: ^{7}Li NMR spectrum of lithium anthraquinone 2,6-bis(sulfamate) (155 MHz, deuterated water). Inlet shows the zoomed spectrum between −0.20 and 0.20 ppm.*

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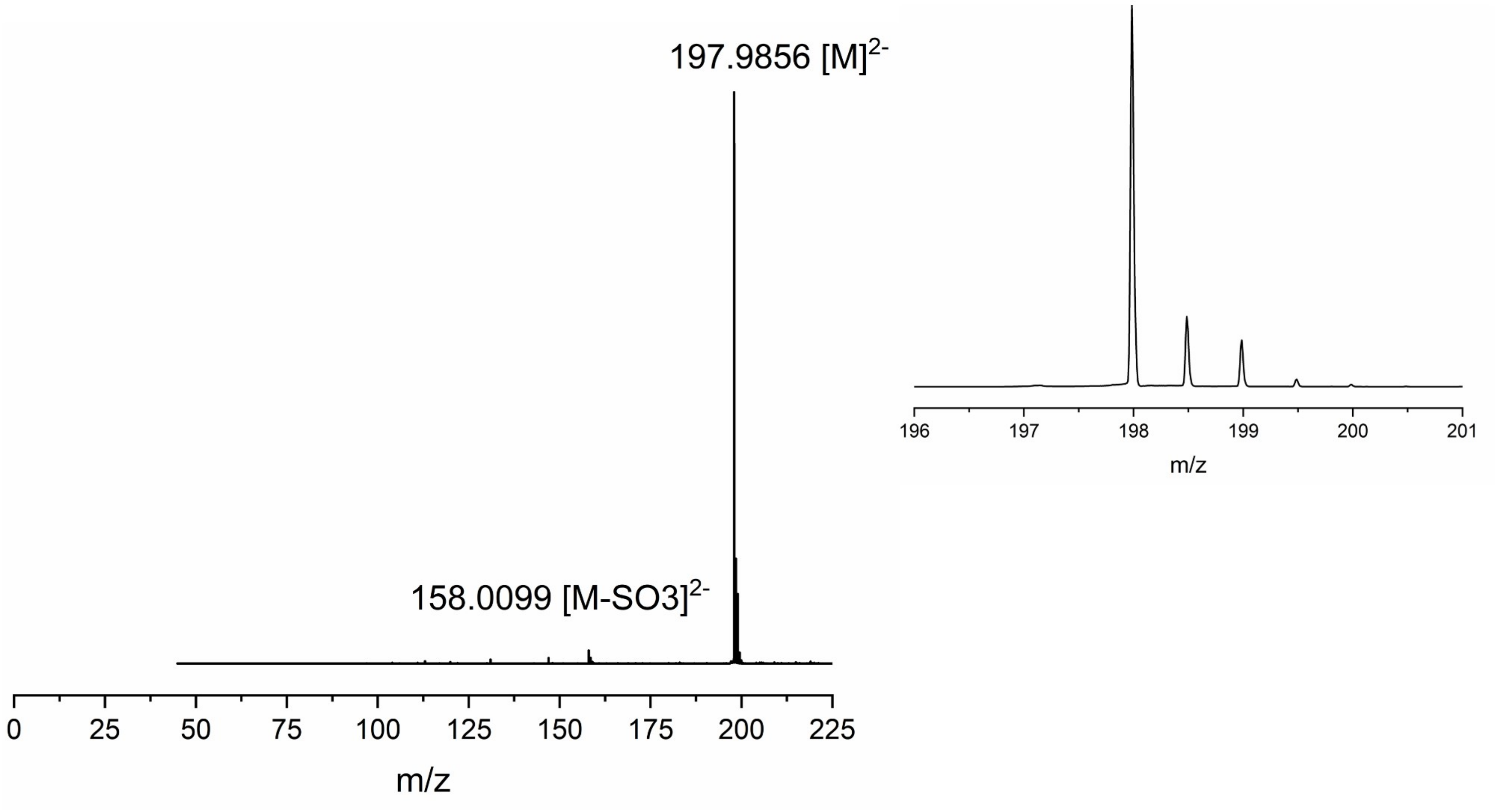


Figure 6: HR-MS spectrum of anthraquinone 2,6-bis(sulfamate). The inlet shows the isotopic pattern of the molecular ion peak.

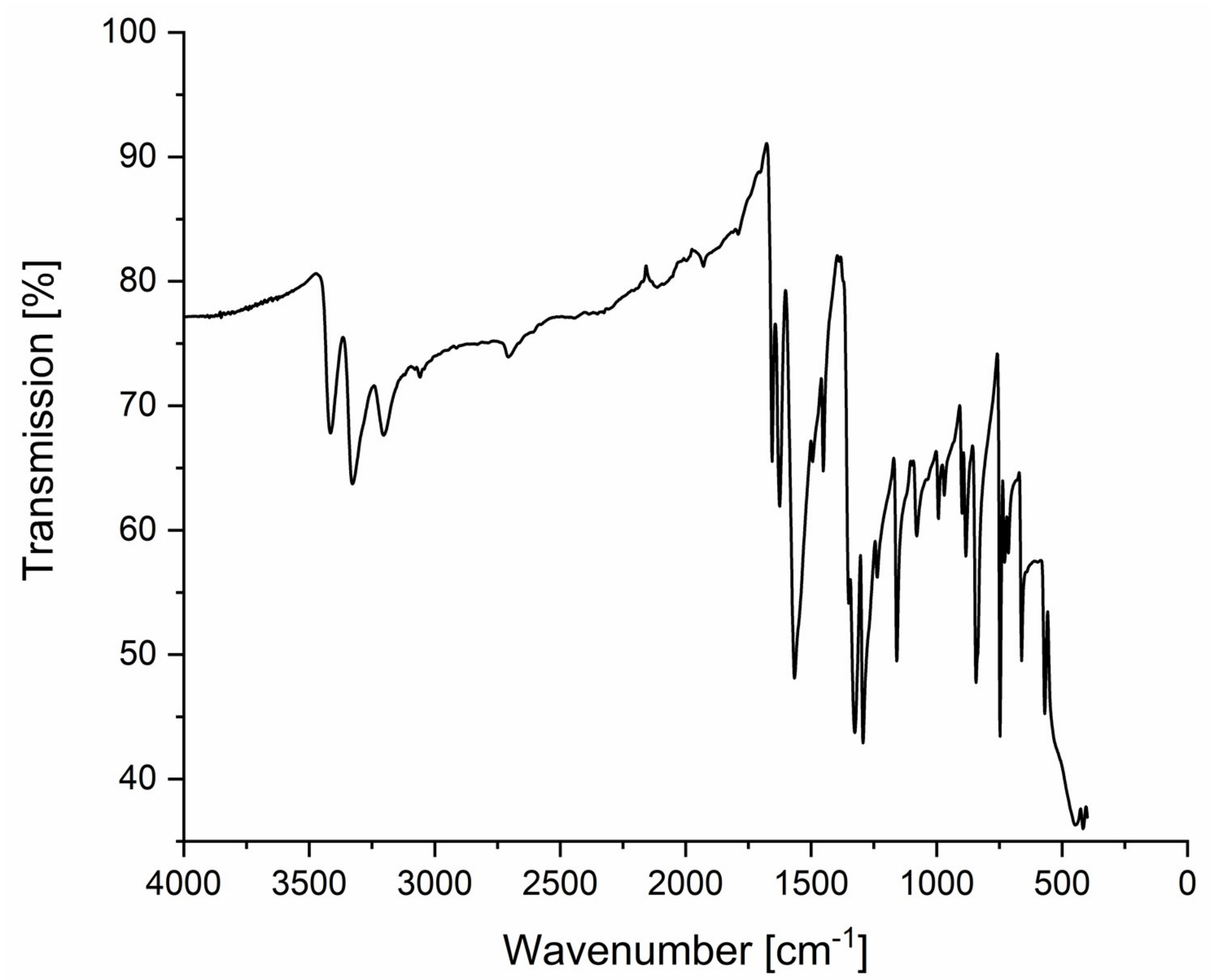
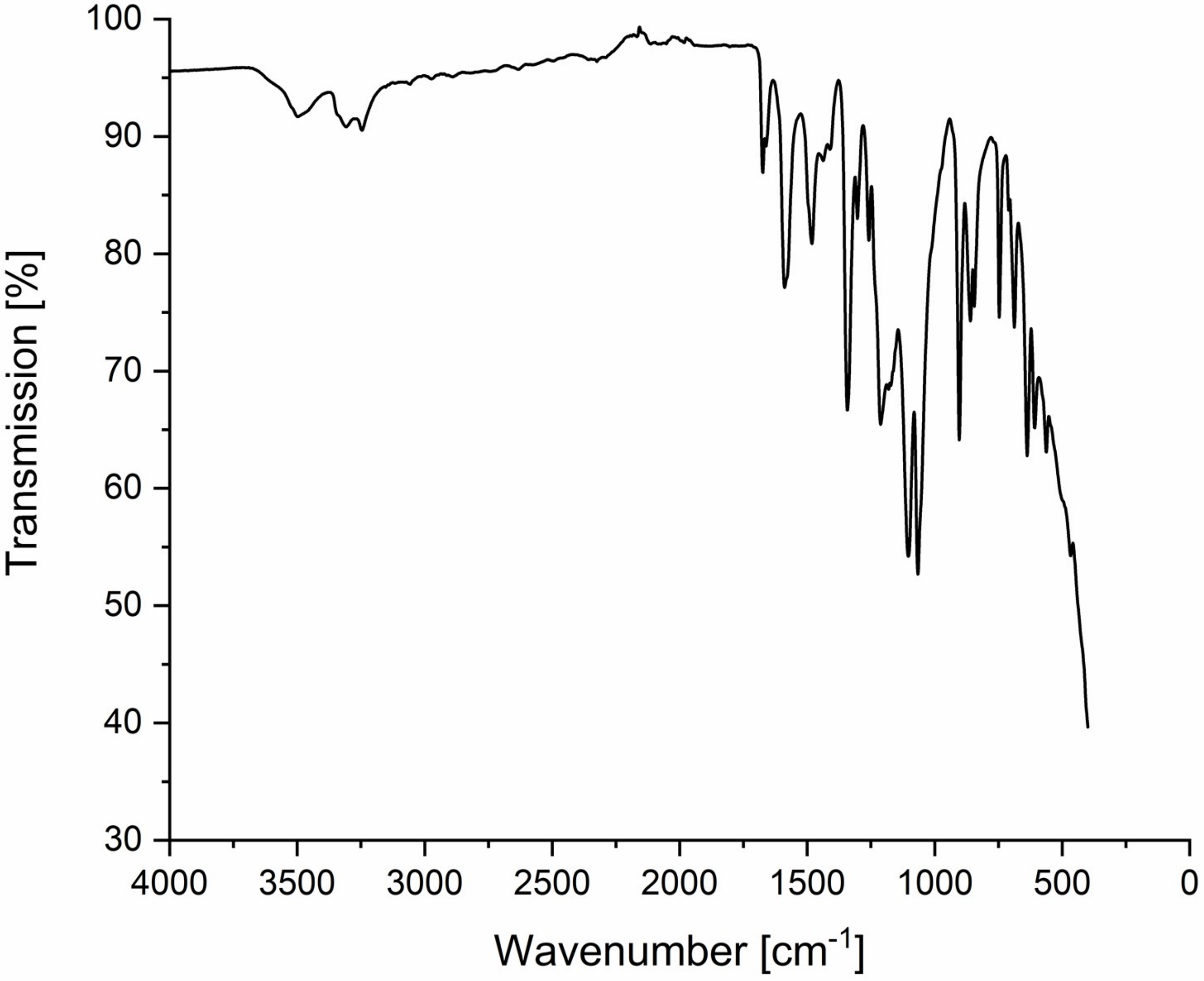


Figure 7: FT-IR spectrum of 2,6-diaminoanthraquinone (Sigma Aldrich).



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94 *Figure 8:FT-IR spectrum of lithium anthraquinone 2,6-bis(sulfamate).*

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Table 2: Summary of the data of the low concentration long term stability test.

Active material concentration [mol L^{-1}]	Volume CLS [mL]	Theoretical capacity CLS [mAh]	Electrolyte composition	Temperature [°C]	Cycle	Current density* [mA cm^{-2}]	Average coulombic efficiency [%]	Decay rate [%d^{-1}]
0.1	15	80.2	0.1 M LiAQS 0.25 M LiOH 1 M LiCl	32	1-50	72 mA cm^{-2}	99.95	0.67
					50	Hold time	-	0.04
					50-100	72 mA cm^{-2}	99.95	0.42
					100	Hold time	-	0.02
					100-150	72 mA cm^{-2}	99.95	0.42
					150	Hold time	-	0.03
					150-200	72 mA cm^{-2}	99.95	0.32
					200	Hold time	-	0.03
					200-250	72 mA cm^{-2}	99.95	0.38
0.1	15	80.2	0.1 M LiAQS 0.25 M LiOH 1 M LiCl	60	1-50	72 mA cm^{-2}	99.95	0.40
					50	Hold time	-	0.04
					50-100	72 mA cm^{-2}	99.95	0.34
					100	Hold time	-	0.03
					100-150	72 mA cm^{-2}	99.95	0.40
					150	Hold time	-	0.04
					150-200	72 mA cm^{-2}	99.95	0.42

* Every cycle consisted of (1) a galvanostatic phase at 72 mAcm^{-2} with an upper limiting voltage of 0.45 V, (2) a potentiostatic phase at 0.45 V with a lower limiting current of 2 mAcm^{-2}, (3) another galvanostatic phase at −72 mAcm^{-2} with a lower limiting voltage of −0.45 V, and (4) another potentiostatic phase at −0.45 V with an upper limiting current of −2 mAcm^{-2}.

Table 3: Summary of the data of the high concentration long term stability test.

Active material concentration [mol L^{-1}]	Volume CLS [mL]	Theoretical capacity CLS [mAh]	Electrolyte composition	Temperature [°C]	Cycle	Current density* [mA cm^{-2}]	Average coulombic efficiency [%]	Decay rate [%d^{-1}]
0.75	10	402	0.75 M LiAQS 0.25 M LiOH 1 M LiCl	32	1-200	80 mA cm^{-2}	100	0.21
0.75	10	402	0.1 M LiAQS 0.25 M LiOH 1 M LiCl	60	1-200	80 mA cm^{-2}	100	0.80

* Every cycle consisted of (1) a galvanostatic phase at 80 mA cm^{-2} with an upper limiting voltage of 0.60 V, (2) a potentiostatic phase at 0.60 V with a lower limiting current of 2 mA cm^{-2}, (3) another galvanostatic phase at −80 mA cm^{-2} with a lower limiting voltage of −0.60 V, and (4) another potentiostatic phase at −0.60 V with an upper limiting current of −2 mA cm^{-2}.

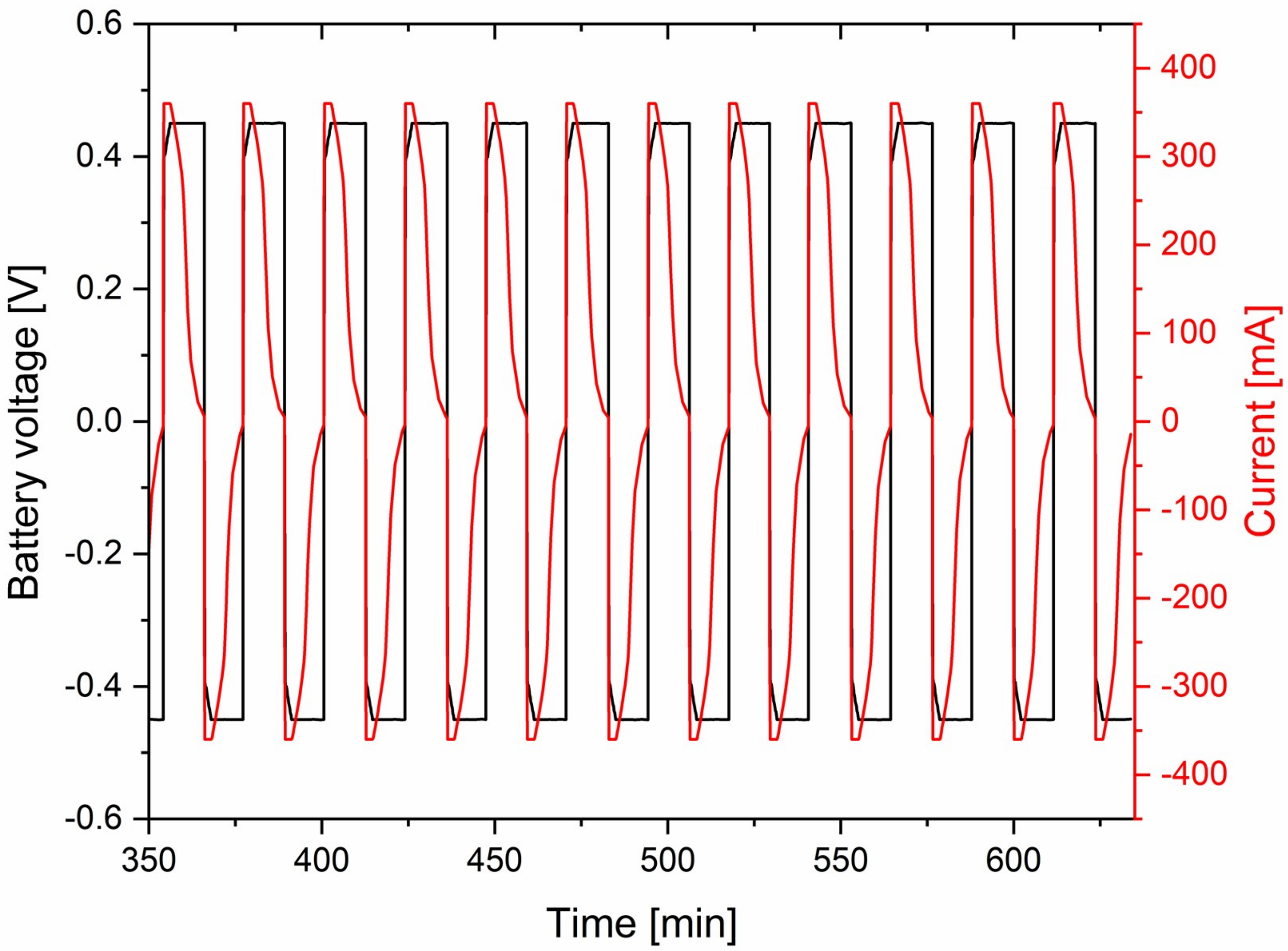

Figure 9: Voltage and current profile of the cycle 11 to 22 of the battery with a 0.1 M LiAQS electrolyte concentration.

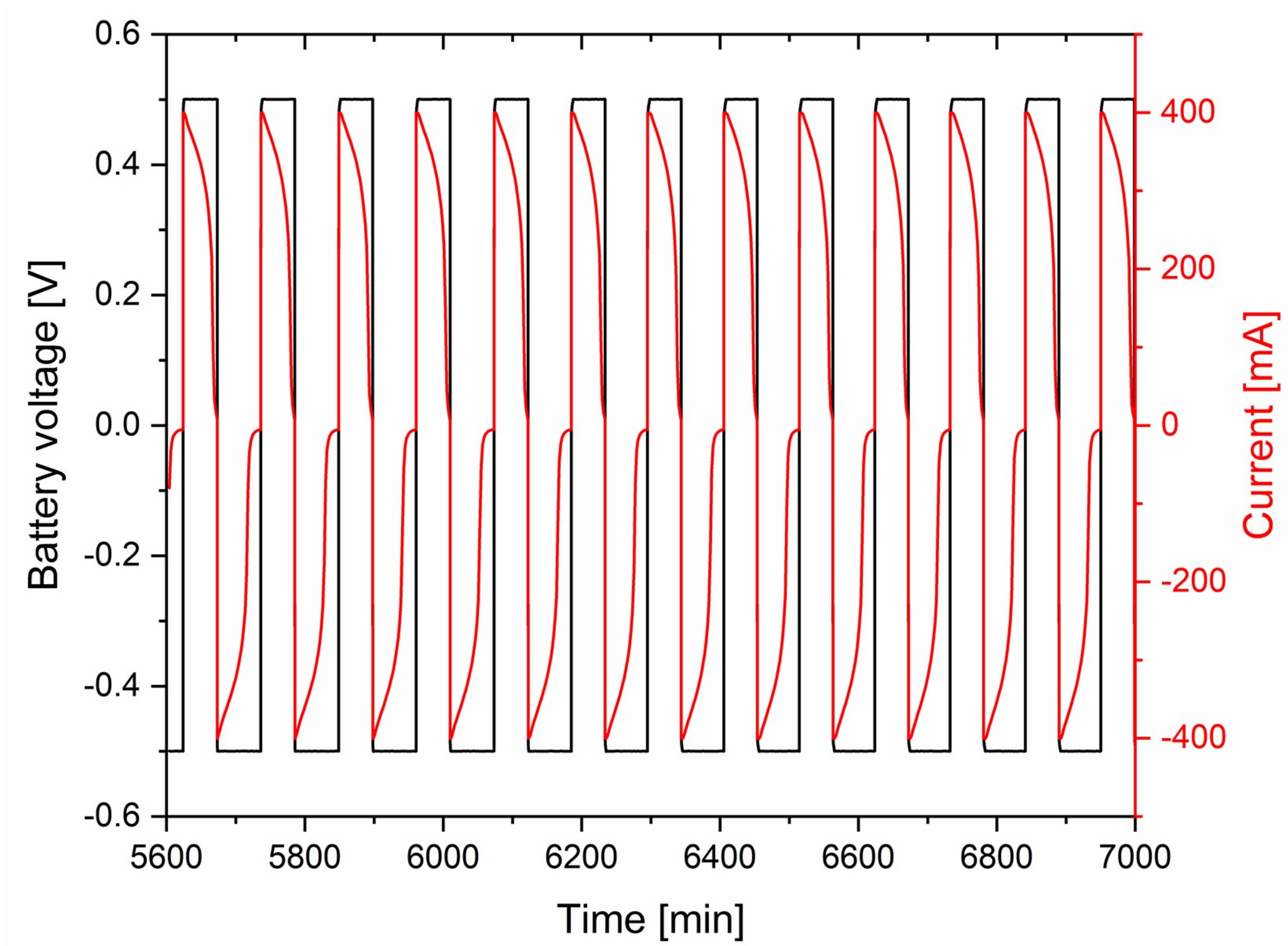

Figure 10: Voltage and Current profile of the cycle 11 to 22 of the battery with a 0.75 M LiAQS electrolyte concentration.

Literature

1. T. Kenny, S. M. Aly, D. Fortin and P. D. Harvey, *Chem. Commun.*, 2012, **48**, 11543-11545.
2. V. Y. Fain, B. E. Zaitsev and M. A. Ryabov, *Russ. J. Gen. Chem.*, 2010, **80**, 550-550.