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Supplementary information for

A comparative study about the suitability of glymes and its derivatives as electrolyte solvents for graphite co-intercalation electrodes in lithium-ion and sodium-ion batteries

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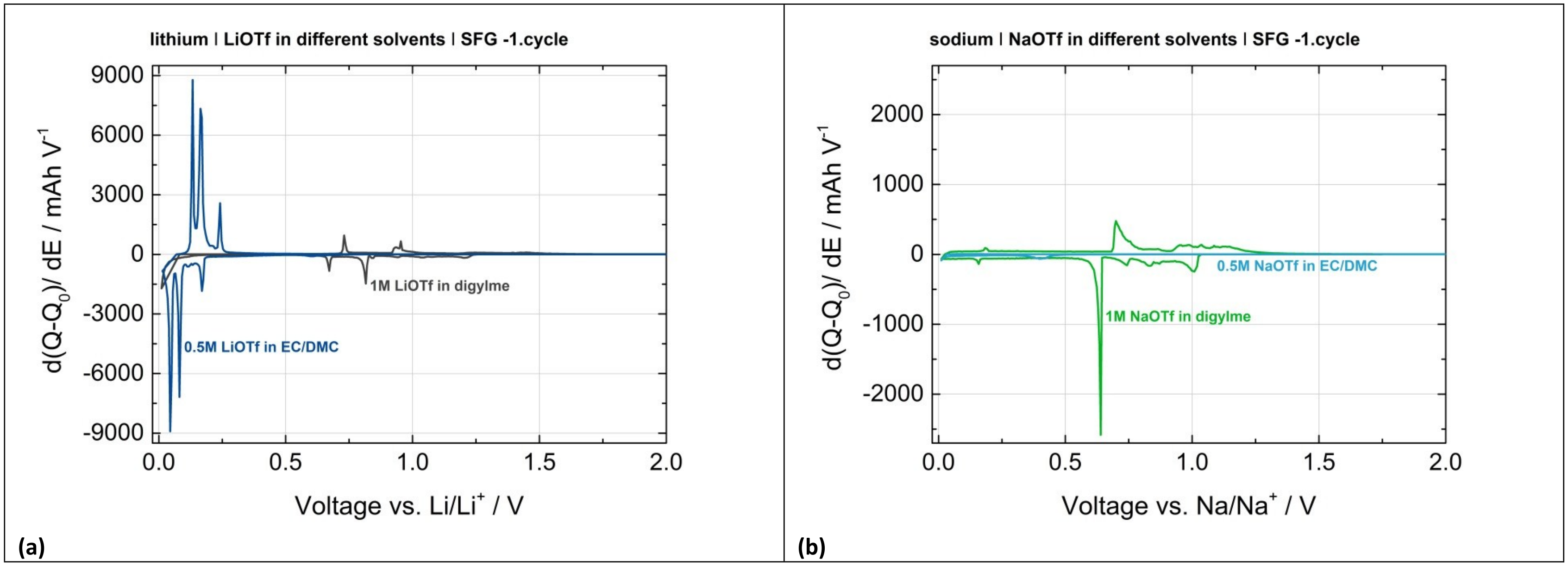
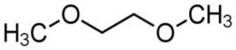
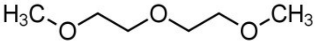
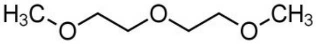
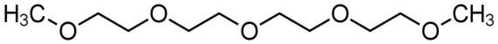


Figure S 1: Differential capacities of graphite as electrode in (a) lithium and (b) sodium cells under usage of 0.5 M A$^+$OTf$^-$ in EC/DMC or 1 M A$^+$OTf$^-$ in diglyme. Data calculated from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with an applied current of 37.2 mA/g.

Table S 1: Structure names, abbreviations, CAS-numbers, structures, purity, viscosity, flash point and relative density of monoglyme, diglyme, triglyme and tetraglyme. All data from *Sigma Aldrich* where the solvents were purchased and used as received.

Name	Abbr.	CAS-no.	Structure	Purity /%	Viscosity /mm^2 s^{-1}	Flash point /°C	Rel. density /g cm^{-3} at 25°C
1,2-Dimethoxyethan	**1G**	110-71-4		99.5	0.5	85	0.8670
Bis(2-methoxyethyl)ether	**2G**	111-96-6		99.5	1.20	162	0.943
Triethylenglykol-dimethylether	**3G**	112-49-2		99.0	2.5	216	0.986
Tetraethylenglykol-dimethylether	**4G**	143-24-8		99.0	4.1	275-276	1.009

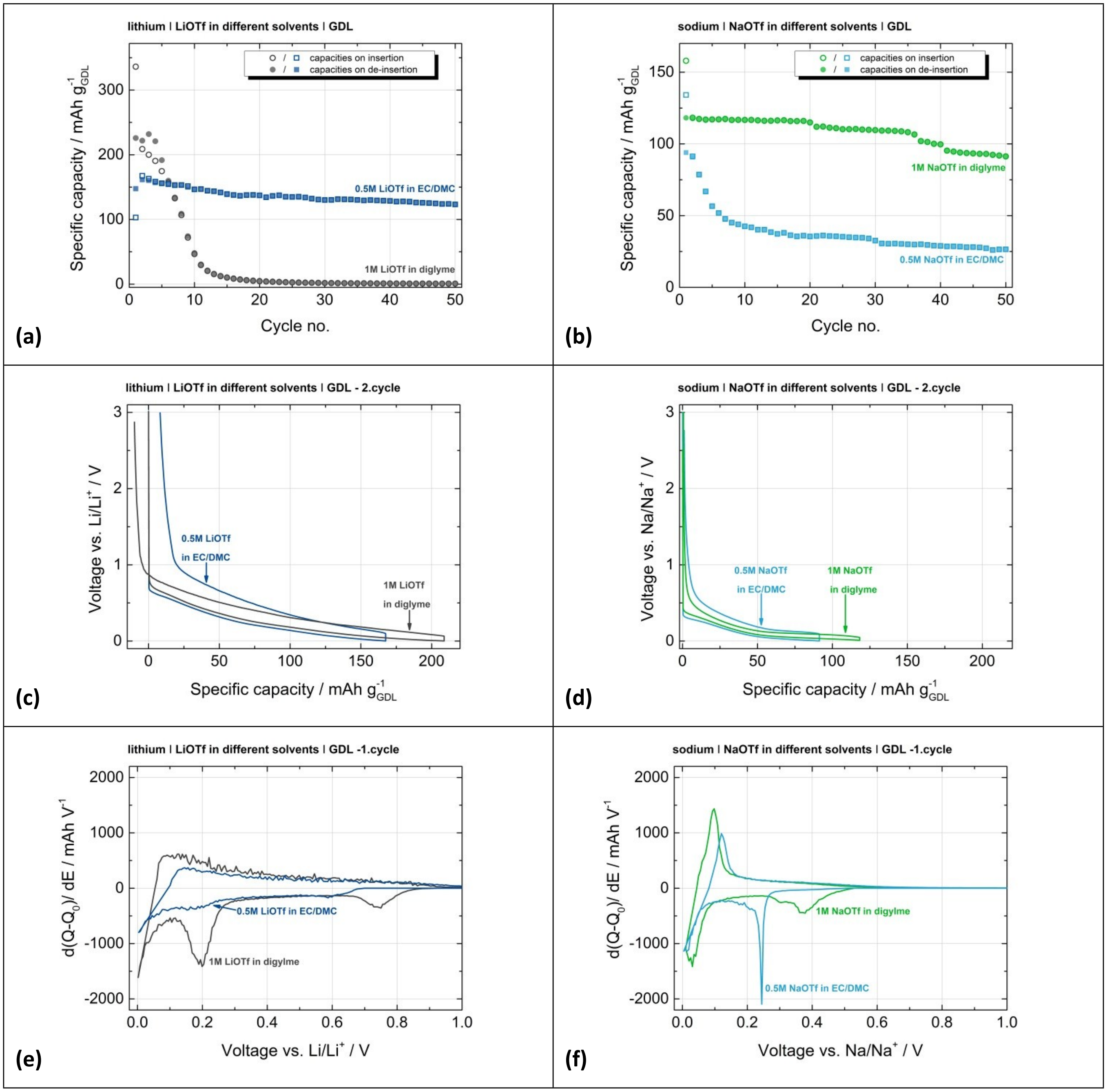


Figure S 2: Electrochemical measurements on non-graphitic carbon as electrode in lithium and sodium cells under usage of 0.5 M A^+OTf^- in EC/DMC or 1 M A^+OTf^- in diglyme. (a)/(b) specific capacities and (c)/(d) voltage characteristics from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with a applied current of 37.2 mA/g. (e)/(f) Differential capacities calculated from the galvanostatic cycling measurements. As non-graphitic carbon a binder-free gas diffusion layer (GDL, Freudenberg H2315, *Quintech*) was used as received.

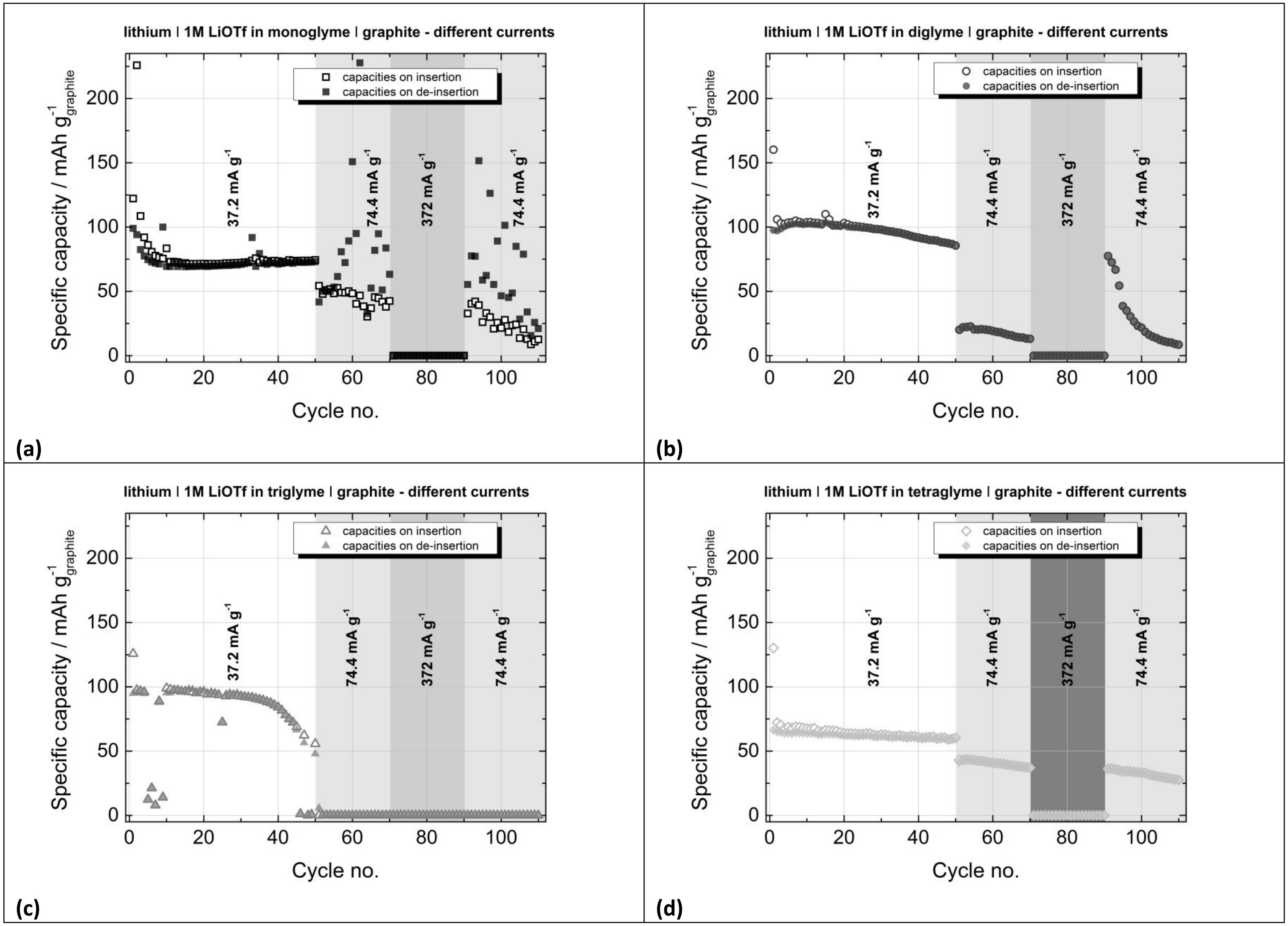


Figure S 3: Specific discharge (i.e. co-intercalation or lithiation step) capacities of the different glymes for lithium half cells recorded at different applied currents in a potential range of 0.01 V-3.0 V. For (a) monoglyme, (b) diglyme, (c) triglyme and (d) tetraglyme used as electrolyte solvent.

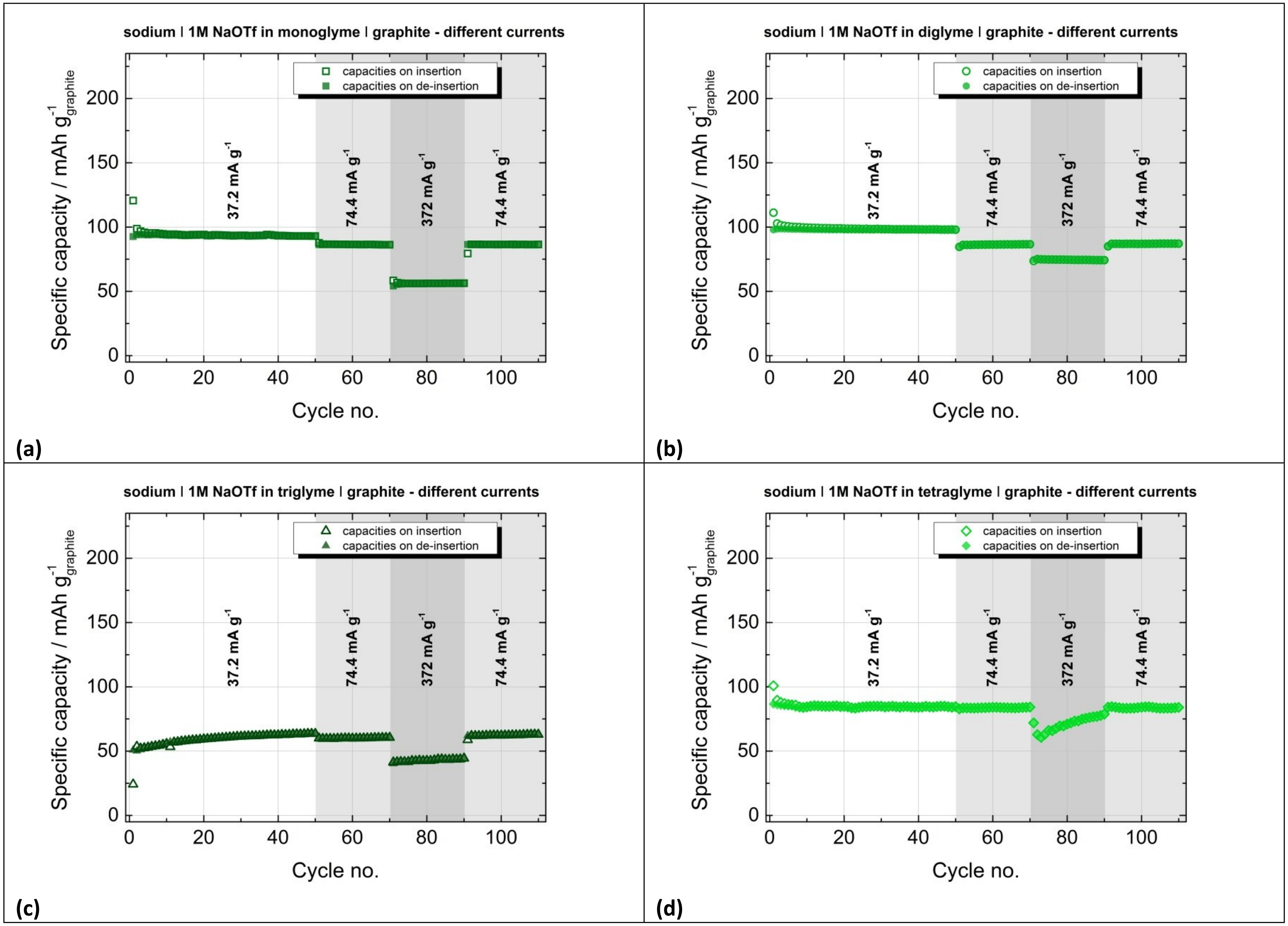


Figure S 4: Specific discharge (i.e. co-intercalation or sodiation step) capacities of the different glymes for sodium half cells recorded at different applied currents in a potential range of 0.01 V-3.0 V. For (a) monoglyme, (b) diglyme, (c) triglyme and (d) tetraglyme used as electrolyte solvent.

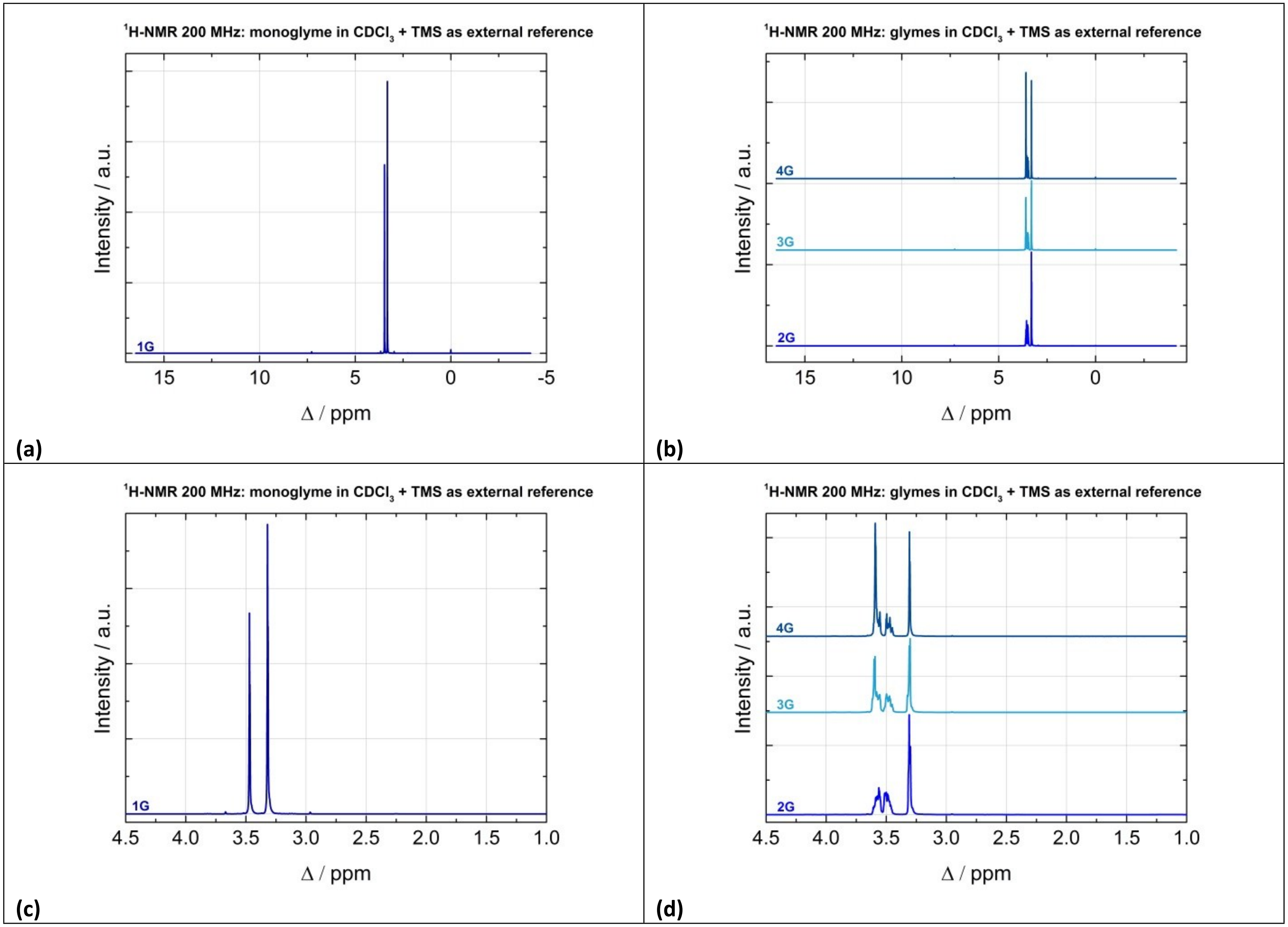
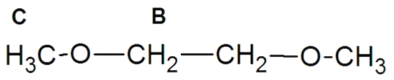


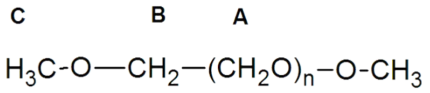
Figure S 5: ^{1}H-NMR 200MHz of the pure glymes (used as received) in CDCl$_3$ with TMS as external standard. (a)/(c) monoglyme (c)/(d) diglyme, triglyme and tetraglyme. No significant amounts of impurities could be determined. Important, the solvents seem to be mainly free of water since the signal at 1.58 which should represent H_2O in CDCl$_3$ is not existent.

monoglyme:



$H_3C\text{-}O\text{—}CH_2\text{—}CH_2\text{—}O\text{-}CH_3$

diglyme, triglyme and tetraglyme:

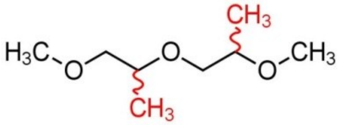
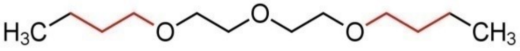
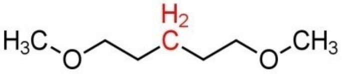


$H_3C\text{-}O\text{—}CH_2\text{—}(CH_2O)_n\text{–}O\text{-}CH_3$ with n= 2, 3, 4

Solvent	(A) CH_2	(B) CH_2	(C) $O\text{-}CH_3$
monoglyme	-	3.52 (s)	3.32 (s)
diglyme	3.60 (m)	3.57 (m)	3.31 (s)
triglyme	3.60 (m)	3.50 (m)	3.30 (s)
tetraglyme	3.60 (m)	3.50 (m)	3.30 (s)

Table S 2: Chemical shifts in ppm. Values validate via comparison with the tables of H. E. Gottlieb, V. Kotlyar, A. Nudelman, 1997, *3263*, 7512–7515.

Table S 3: Structure names, abbreviations, CAS-numbers, structures, purity, viscosity, flash point and relative density of diglyme, DPGDME, Butyl-2G and 1,5-DMP. All data from Sigma Aldrich where the solvents were purchased.

Name	Abbr.	CAS-no.	Structure	Purity /%	Viscosity /mm^2 s^{-1}	Flash point /°C	Rel. density /g cm^{-3} at 25°C
Bis(2-methoxyethyl)ether	**2G**	111-96-6		99.5	1.20	162	0.943
Bis(methoxypropyl)ether	**DPGDME**	111109-77-4		99.0	1.12	74	0.951
Bis(2-butoxyethyl)ether	**Butyl-2G**	112-73-2		99.0	2.3	118	0.885
1,5-Dimethoxypentane	**1,5-DMP**	111-89-7		98.0	No data available	60	0.843

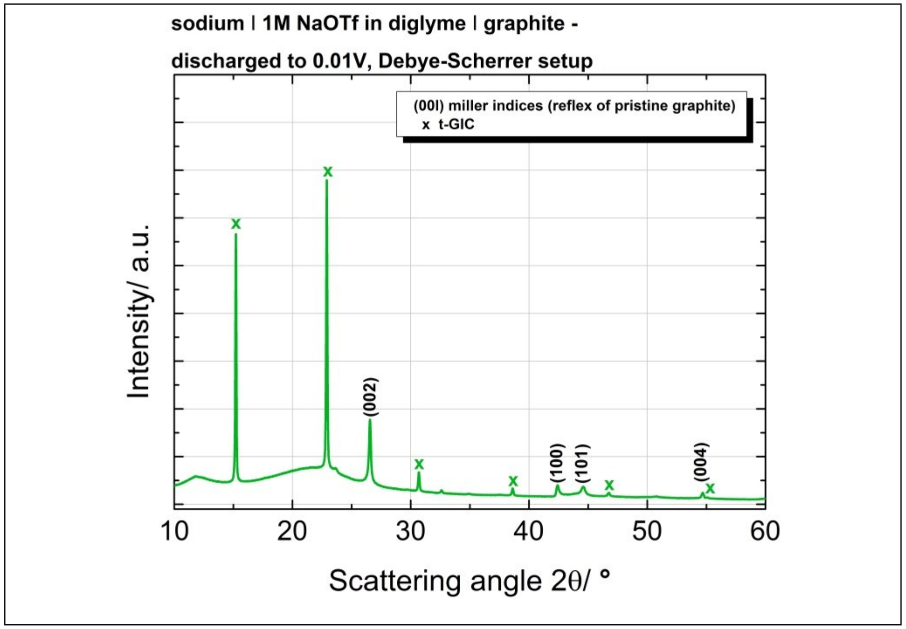


Figure S 6: Results from X-ray diffraction using the Debye-Scherrer setup. Chemical preparation of the ternary graphite intercalation compound was done after the preparation route described by Mizutani *et al.*[1] Thereto 0.01 mmol of naphthalene (*Sigma Aldrich*) were mixed with 6 mmol of sodium (*BASF*) and 11 mmol graphite (SFG-44, *TIMCAL Graphite*). Then 6 mL of diglyme (*Sigma Aldrich*) were added and the solution was stirred over 24 h under argon atmosphere to ensure a complete reaction of the material. The so co-intercalated graphite was filtrated and dried and afterwards filled into a quartz tube inside the glovebox and sealed air-tight with vacuum grease. After transferring the tube outside the glovebox the tube was fused. The diffraction pattern were taken in an angular range of $2\theta=5°-80°$ (step width of $2\theta=0.02°$, step time 60s) with a *Stoe transmission diffractometer System STADI P from Stoe & Cie GmbH, Darmstadt* with a Cu-K_{α}=1.5413 Å (40 kV, 40 mA) and were analyzed with *WinXPOW*. The diffraction pattern exhibits reflexes of the stage-1 and stage-2 *t*-GICs of Na-diglyme and domains of pristine graphite due to an incomplete co-intercalation reaction of the used graphite material. In contrast to the diffraction patterns recorded under reflection using the Kapton tape the intensities of the main reflex (here denoted as (001), (002) and (003)) are much higher. The reflexes are not labeled with Miller Indices but instead with the denotation of Dresselhaus et al..[2] From these results it can be concluded that it is sufficient to measure the co-intercalated samples under Kapton tape as sealing since it solely leads to a minor loss in reflex intensity but it is much easier to handle.

[1] Y. Mizutani, T. Abe, M. Inaba, Z. Ogumi, *Synth. Met.* 2002, *125*, 153–159.

[2] M. S. Dresselhaus, G. Dresselhaus, in *Adv. Phys.*, Taylor And Francis, London, 1981, pp. 139–326

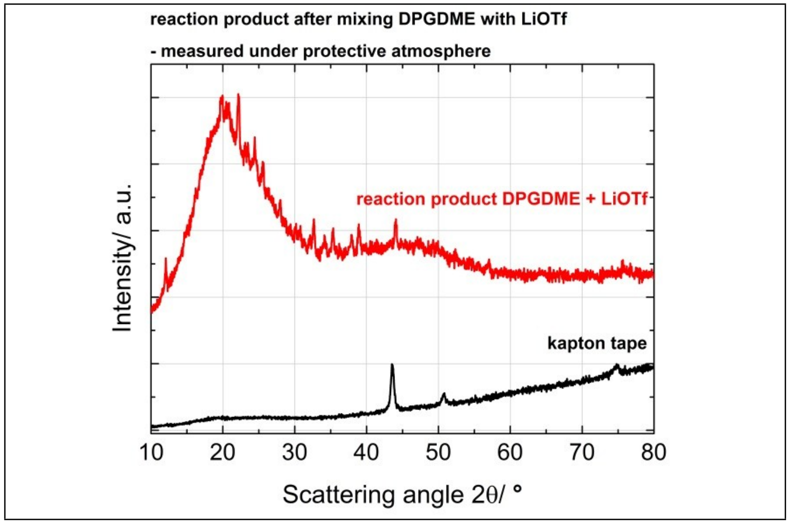


Figure S 7: Top: X-ray diffraction pattern of the reaction product after mixing DPGDME and 1M LiOTf. Bottom: diffraction pattern the Kapton tape that was used to protect the samples from air.

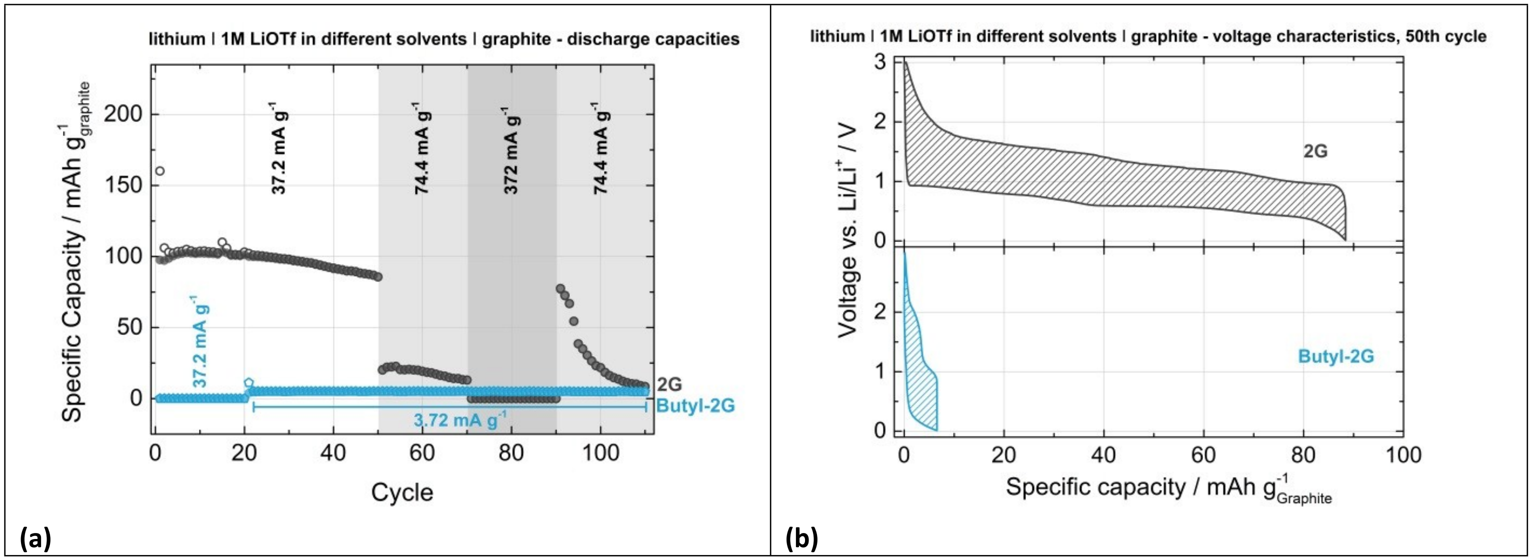


Figure S 8: (a)/(b) Electrochemical measurements and (d) X-ray diffraction pattern of co-intercalated graphite electrodes in lithium cells while using Butyl-2G and 2G as electrolytes solvents and with different applied currents. (a) Specific capacities and (b) voltage characteristics in the 50th from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V.

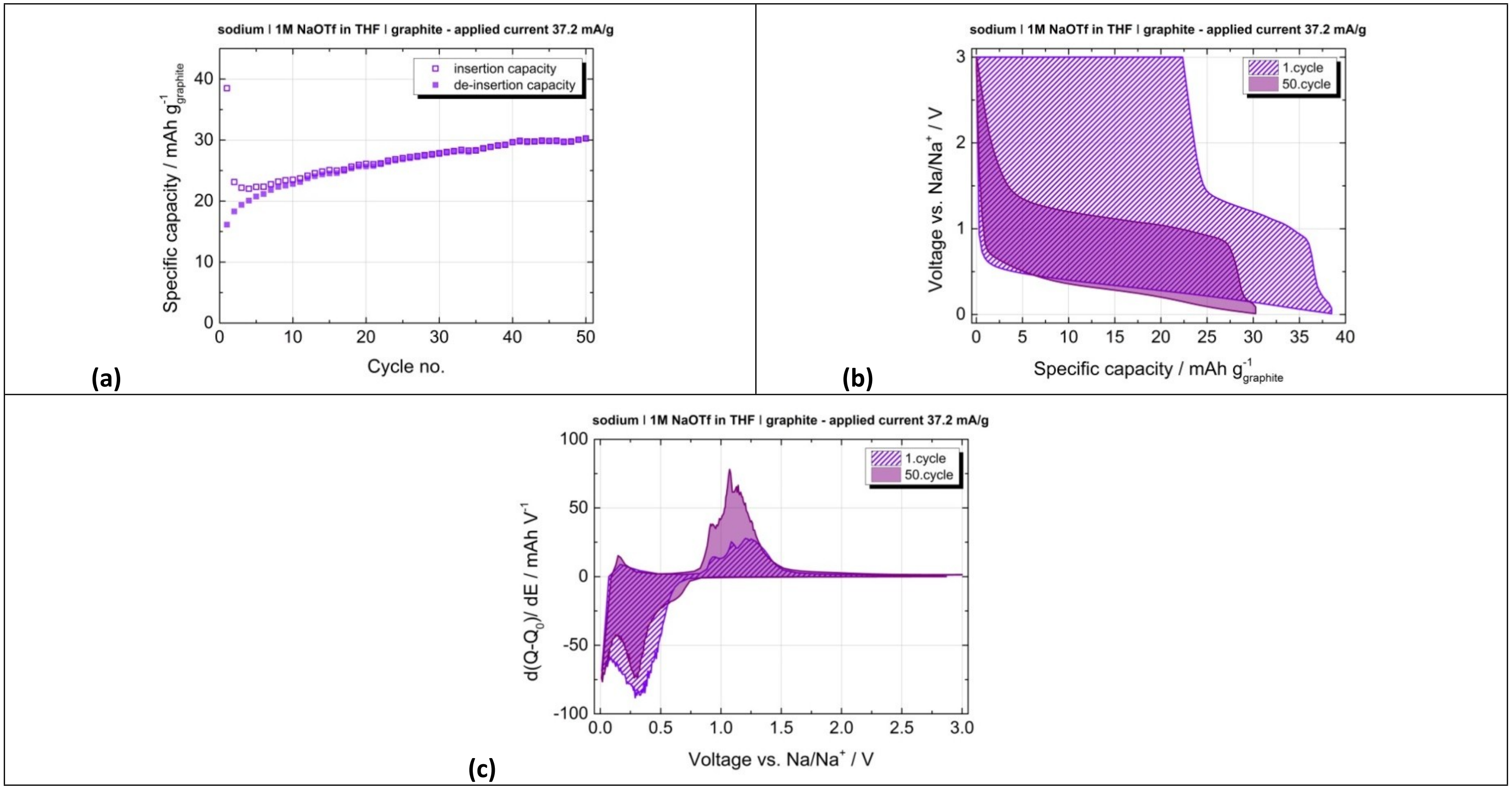


Figure S 9: Electrochemical co-intercalated (sodiated) graphite electrode in a sodium half-cell while using THF as electrolyte solvent. (a) Specific capacities and (b) voltage characteristics derived from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with an applied current of 37.2 mA/g. (c) Differential capacities of graphite as electrode in a sodium half-cell under usage of 1 M NaOTf in THF. Calculated from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with an applied current of 37.2 mA/g. Specific capacities are low in this case but steadily increase to around 30 mAh/g after prolonged cycling (Figure 14a). This behaviour might be related to an activation process of the graphite electrode, such as mechanical expansion, due to the fact that a complex consisting of one or more THF-molecules and a sodium ion is spatially more complicated and not as spherical as in the case of certain glymes, for example.(26,30,49–51). The poor kinetics can be also seen from the large hysteresis of the voltage profile (Figure 14b). Noticeable is the irreversible capacity in the first few cycles. With values of 22 mAh/g it is comparable to the irreversible capacities of the glyme-based und DPGDME-based electrolytes. The irreversible losses are therefore likely intrinsic and linked to irreversible reactions between the graphite surface, the ether segments of the solvents and/or the conductive salt (or its impurities). The corresponding graph of the differential capacity is shown in the supplementary information and exhibits similar staging mechanism as the DPGDME-based cells (see supplementary information figure S9).

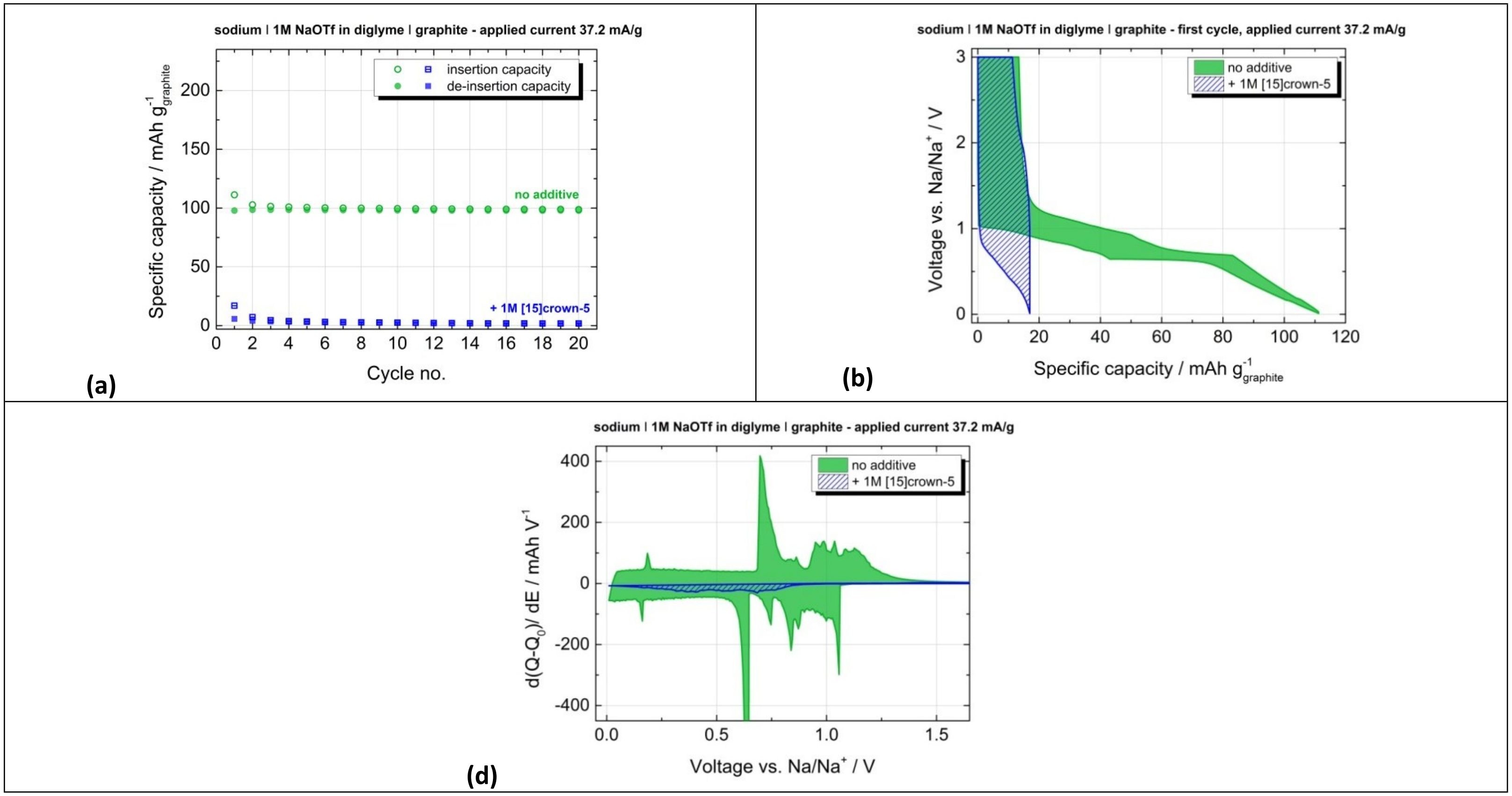


Figure S 10: Electrochemical cycled graphite electrodes in sodium cells while using diglyme or diglyme + 1M [15]crown-5 as electrolyte solvent. (a) Specific capacities and (b) voltage characteristics from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with an applied current of 37.2 mA/g. (c) Differential capacities of graphite as electrodes in sodium cells under usage of 1 M NaOTf in diglyme with and without addition of 1M of the additive [15]-crown-5. Calculated from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with an applied current of 37.2 mA/g. Due to the chemical similarity to the linear glymes circular [15]crown-5 was tested as an additional solvent. Due to its circular structure it is known to form very stable sodium ion-crown ether complexes.(43,44) Since it is not possible to dissolve the conductive salt in the pure crown-ether as single solvent, we added the crown-ether into an diglyme-based electrolyte. We assume that the crown-ether complexes are stronger compared to 2G and added just as much [15]crown-5 to complex all sodium ions in a 1M NaOTf/2G electrolyte. As a result, we surprisingly found virtually no electrochemical activity. The specific capacity was below 2 mAh/g upon cycling (Figure S10). As the chemical structures of both solvents are nevertheless similar, the reason for the poor electrochemical activity in the case of [15]crown-5 might be again related to a non-ideal geometry of the solvation shell. Indeed the solvation shell of is non-spherical and much more rigid as compared to the glymes.

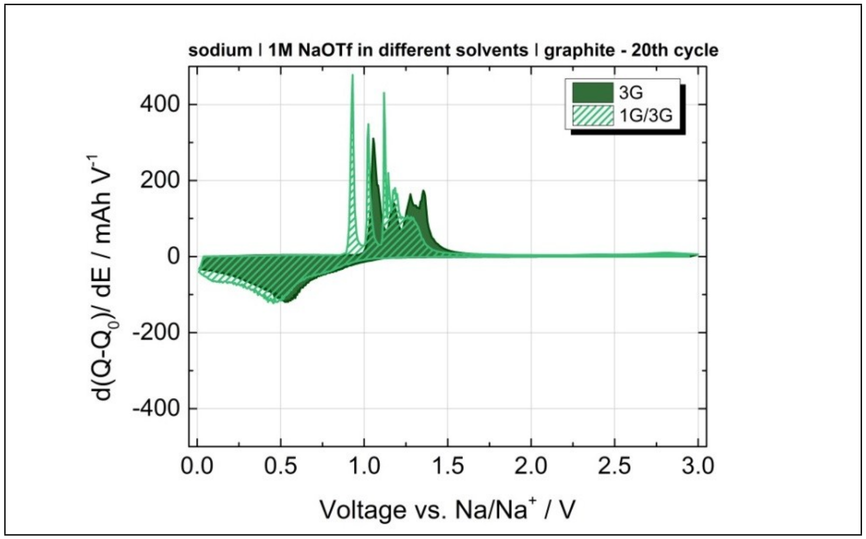


Figure S 11: : Differential capacities of graphite as electrode in sodium cells under usage of 1 M NaOTf in triglyme or a mixture of monoglyme and triglyme (1:1). Calculated from galvanostatic cycling measurements in a potential range of 0.01 V-3.0 V with an applied current of 37.2 mA/g.

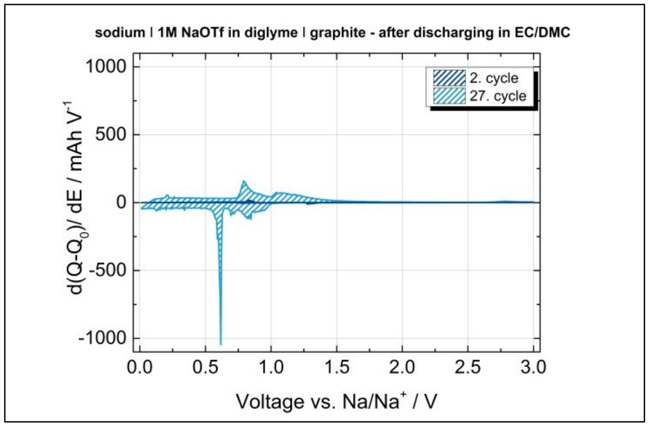


Figure S 12: Differential capacities plots from galvanostatic cycling measurements in the second and 27th of a graphite electrodes after it was discharged (sodiation step) in a carbonate-based electrolyte to form a SEI-layer on its surface in sodium cells in a potential range of 0.01 V-3.0 V with a applied current of 37.2 mA/g.