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# 3-Pentadecyl-2,4-dioxo-16-crown-5 as a promising additive in electrolytes for chemical power sources

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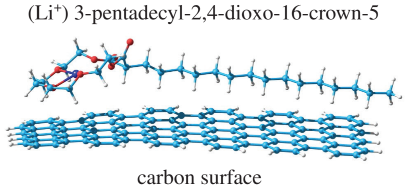
**A new crown ether, 3-pentadecyl-2,4-dioxo-16-crown-5, with surfactant properties has been synthesized in three simple steps from diethyl pentadecylmalonate. Quantum chemical calculations show that this crown ether is capable of adsorbing both on the surface of the lithium anode and on the surface of carbon. The effectiveness of its application as a functional additive in organic electrolyte for lithium batteries has been experimentally confirmed.**



*Keywords*: crown ethers, lithium ions, organic electrolyte, quantum-chemical modeling, electrochemical impedance, charge-discharge cycling, lithium battery, lithium ferro phosphate cathode.

The developers of new chemical power sources are always faced with the problem of eliminating secondary electrochemical reactions that run parallel to the main electrode ones thus interfering the operation of the batteries. One approach to solve this problem is to create a protective layer that would pass only metal cations ($Li^+$, $Na^+$, $K^+$, *etc.*) and would be impervious to molecules of an organic solvent.

For this purpose, a new crown ether, *viz.* 3-pentadecyl-2,4-dioxo-16-crown-5 **1**, containing both the crown ether cavity and long-chained pentadecyl substituent was obtained in this work. Previously, synthesis of similar derivatives with shorter substituents such as Ph, $n$-$C_8H_{17}$ and $n$-$C_{12}H_{25}$ was reported.[1,2] As functional additives, these compounds have not been studied, although crown ethers are known to be good ion complexing agents[3] improving electrochemical properties of various materials.[4–8]

At the first stage of the work, a theoretical study was conducted to appreciate the possibility of adsorption of crown ether **1** on surfaces of the two anode materials most common to date, namely, lithium metal and carbon. As a model of lithium metal, a cluster $Li_{72}$ was used; the carbon was modeled by a graphite surface of $10^8$ atoms. For theoretical calculations, the non-empirical exchange-correlation Perdew, Burke and Ernzerhof (PBE) functional[9] and the extended basis H [6s2p/2s1p], C, O [10s7p3d/3s2p1d], Li [10s7p3d/4s3p1d] were used.[†] On the surface of the lithium anode, compound **1** is adsorbed by the crown ether cavity [Figure 1(*a*)], so the lithium atom moves from the surface of the anode being coordinated in the cavity. The energy release in this process is 25.8 kcal mol$^{-1}$, which indicates its profitability. Examination of the adsorption of crown ether **1** on the carbon surface has shown that it can be adsorbed by three ways, namely, with a macrocycle (the energy gain of 1.9 kcal mol$^{-1}$), with the pentadecyl substituent (the energy gain of 7.7 kcal mol$^{-1}$) and simultaneously with macrocycle and alkyl moieties (the energy gain of 4.1 kcal mol$^{-1}$). The adsorption energy of the $Li^+$ ion with **1**@C complex is 16.6 kcal mol$^{-1}$. As for adsorption of $Li^+$–**1** complex on the carbon surface [Figure 1(*b*)], the adsorption energies are practically independent of the manner of compound **1** attachment.

Taking into account the theoretical conclusions about the profitability of the adsorption of crown ether **1**, we performed its synthesis and studied its effect as an additive on the operation of electrochemical cells.

The synthesis of compound **1** involved three consecutive stages (Scheme 1). Known intermediates **2** and **3** were prepared

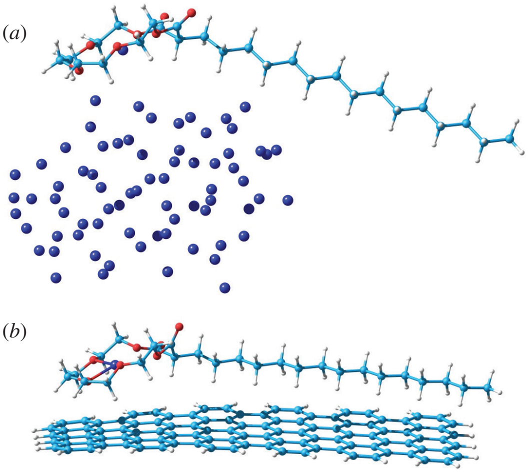


**Figure 1** Optimized structures of adsorbed complexes of compound **1** with a coordinated $Li^+$ ion on the surface of (*a*) lithium metal, (*b*) carbon.

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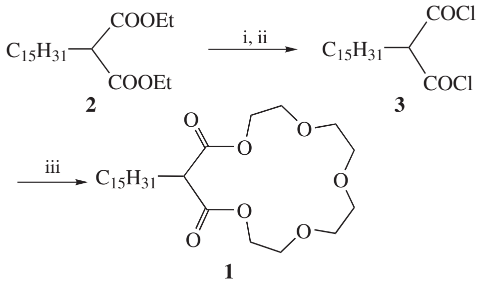
[†] All calculations were performed using the PRIRODA software package[10] and the computational capabilities of the Joint Supercomputer Center of the Russian Academy of Sciences, Moscow.



**Scheme 1** *Reagents and conditions*: i, NaOH, $H_2O$, 50–55 °C, 2 h, then $H^+$ (20% HCl); ii, $SOCl_2$, benzene, 60–65 °C, 5 h; iii, $HO(CH_2CH_2O)_4H$, benzene, 60–70 °C, 15 h.

as described.[11,12] Final product **1** was obtained analogously to reported procedures[13.14] with slight changes.[‡]

Crown ether **1** was tested as an additive (5 wt%) in a 1 M $LiPF_6$ liquid electrolyte in 1 : 1 ethylene carbonate/dimethyl carbonate (EC/DMC) mixture with a water content of $5\times10^{-3}$ %. In a glove box with an atmosphere of dry argon, symmetrical Li // Li cells were assembled in sealed button cases (electrode diameter of 17 mm). Their impedance was recorded on the first day and after storage for 8 months at room temperature.[§] Equivalent schemes were selected for these hodographs, and the calculations were performed using the ZView2 program. The results are illustrated in Figure 2 and Table 1.

The resistance of solid electrolyte interphase (SEI) in the case of the addition of crown ether is lower (see Table 1), but a layer of adsorbed crown ether molecules also promotes an increase in impedance. It decreases with time, which indicates the ordering of the crown ether molecules. This layer may interfere with the contact of solvent molecules and with the surface of the electrode (*cf.* data in refs. 15,16), which allows us to hope for an improvement in the performance of the battery.

The next stage of the work was the study of the effect of compound **1** additives on the operation of Li // $LiFePO_4$ battery prototypes.[¶] The charge–discharge profiles are shown in Figure 3.

**Table 1** Parameters of the equivalent circuit calculated for the hodographs of Li // Li cells.[a]

| Electrolyte | Storage time/ months | *R*/Ohm | | |
|---|---|---|---|---|
| | | electrolyte | SEI | crown ether layer |
| without additives | 0 | 2.2 | 940 | – |
| without additives | 8 | 4.7 | 1260 | – |
| with compound **1** | 0 | 1.2 | 330 | 909 |
| with compound **1** | 8 | 1.6 | 860 | 625 |

[a] A complete calculation of the equivalent circuit parameters is given in Table S2 (see Online Supplementary Materials).

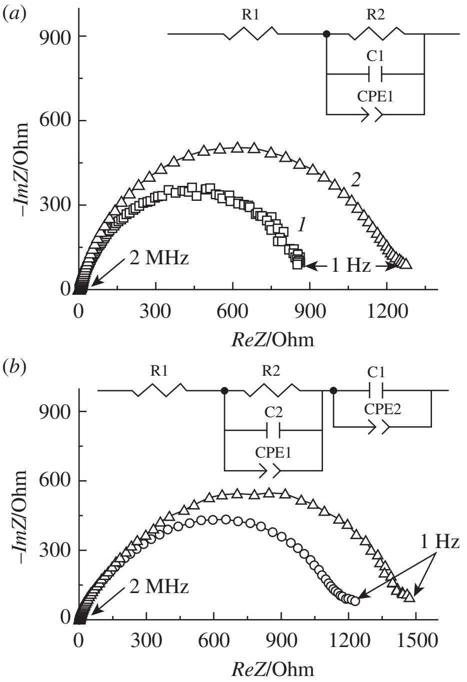


**Figure 2** Hodographs of impedance of Li // Li cells with electrolyte (*a*) without additives and (*b*) with compound **1**. In the equivalent circuits corresponding to the hodographs, R1 is the electrolyte resistance, R2 is the SEI resistance at the Li / electrolyte interface, C1 is the capacity of the double electric layer, C2 is the capacity of the double electric layer of the adsorbed crown ether layer, CPE1 and CPE2 are the elements with a constant phase angle. Curves *1* stand for results after the first day, curves *2* for results after 8 months of storage at room temperature.

The addition of crown ether **1** to the electrolyte brings the charging and discharge capacity within 80 cycles to the same value, in contrast to the initial electrolyte where the charging capacity exceeds the discharge capacity by 20 mA h $g^{-1}$.

At the initial stage of testing prototype batteries (see Figure 3, curves *1* and *3*), the effect of the addition of crown ether **1** does not appear because the bulk layer of crown ethers, apparently, has not yet acquired an optimal packing, which complicates the electrode reaction. At the 80th cycle, the charge–discharge profiles undergo changes, which reveals the positive effect of crown ether (curves *2* and *4*).

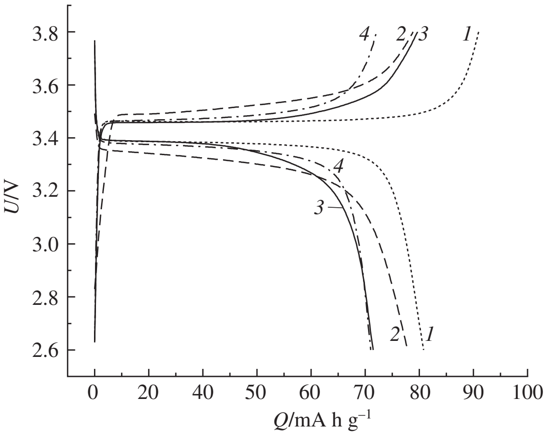


**Figure 3** Charge–discharge profiles for Li // $LiFePO_4$ prototypes with 1 M $LiPF_6$ in EC/DMC (1 : 1) mixture for the (*1*) 2nd and (*2*) 80th cycles without additive **1** and for the (*3*) 2nd and (*4*) 80th cycles with 5 wt% compound **1** at C/10 rate.

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[‡] *15-Pentadecyl-1,4,7,10,13-pentaoxacyclohexadecane-14,16-dione* **1**. Solutions of pentadecylmalonyl chloride **3** (7.0 g, 20 mmol) and tetraethylene glycol (3.88 g, 20 mmol) in benzene (50 ml each) were added separately and at the same rate to stirred anhydrous benzene (300 ml) at 60–70 °C within 3 h. Then the mixture was stirred for more 12 h, the solvent was removed under reduced pressure, and the remaining oil was extracted with hot hexane (300 ml). The yield of product **1** was 8.12 g (43%), white crystalline powder, mp 40–41 °C. For its elemental analysis and solid state $^1$H NMR and $^{13}$C NMR spectra, see Online Supplementary Materials. FT-IR ($\nu$/cm$^{-1}$): 3100, 2990, 2943, 2895, 1731, 1720, 1380, 1305, 1272, 1260, 1132, 1128, 1047, 960, 838, 695.

[§] Electrochemical impedance was measured using an Elins impedance meter Z-2000 (Russia), with a frequency interval of 1–$2\times10^5$ Hz and the amplitude of signal 10 mV.

[¶] A cathode based on $LiFePO_4$ (MTI Corp., USA) was manufactured according to the published procedure.[17] Resource tests for charge–discharge of these prototypes with electrolytes of 1 M $LiPF_6$ in EC/DMC (1 : 1) mixture without and with 5 wt% crown ether **1** were performed on an 8-channel BTS-5V10mA cycler (Neware Technology Ltd., China).

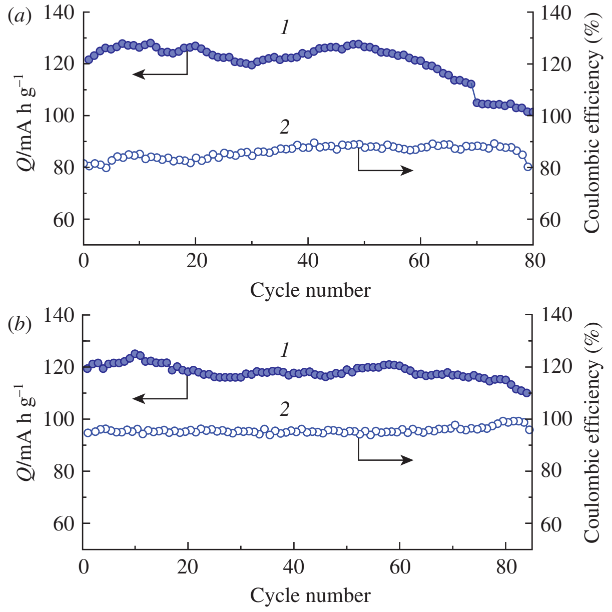

**Figure 4** The dependence of the (*1*) discharge capacity and (*2*) Coulombic efficiency on the charge–discharge cycle number for a prototype with 1 M LiPF$_6$ in EC/DMC (1 : 1) mixture (*a*) without an additive and (*b*) with addition of 5 wt% compound **1**.

Figure 4 shows that due to addition of crown ether **1** the operation of the battery becomes more stable and the Coulombic efficiency reaches almost 100%, with the exception of the first 10 forming cycles where crown ether molecules undergo pre-organization.

In summary, 3-pentadecyl-2,4-dioxo-16-crown-5 is a promising additive for organic electrolytes to improve a stability of lithium batteries. This compound is supposed for further testing in other types of batteries.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.026.

## References

1 M. D. Thompson, J. S. Bradshaw, S. F. Nielsen, C. T. Bishop, F. T. Cox, P. E Fore, G. E. Maas, R. M. Izatt and J. J. Christensen, *Tetrahedron*, 1977, **33**, 3313.
2 P. Geneste, A. Guida, C. Reminiac, G. Amblard and C. Gavach, *Tetrahedron Lett.*, 1981, **22**, 1397.
3 V. P. Solov'ev and A. Y. Tsivadze, *Prot. Met. Phys. Chem. Surf.*, 2015, **51**, 1.
4 K. Ichihashi, D. Konno, T. Date, T. Nishimura, K.Yu. Maryunina, K. Inoue, T. Nakaya, K. Toyoda, Y. Tatewaki, T. Akutagawa, T. Nakamura and S. Nishihara, *Chem. Mater.*, 2018, **30**, 7130.
5 O. V. Yarmolenko, G. Z. Tulibaeva, K. G. Khatmullina, L. M. Bogdanova and A. F. Shestakov, *Mendeleev Commun.*, 2016, **26**, 407.
6 A. A. Ignatova, O. V. Yarmolenko, G. Z. Tulibaeva, A. F. Shestakov and S. A. Fateev, *J. Power Sources*, 2016, **309**, 116.
7 A.-C. Gentschev, H. Hain, S. Scharner and B. Stiaszny, *Patent WO 2017216149A1*, 2017.
8 J. Y. Hwang and H. Y. Ha, *Patent KR 2018001967*, 2018.
9 P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
10 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
11 B. D. Sharma and A. B. Biswas, *Anal. Chem.*, 1958, **30**, 1356.
12 M. J. Pugia, B. E. Knudsen and R. A. Bartsch, *J. Org. Chem.*, 1987, **52**, 2617.
13 J. S. Bradshaw, L. D. Hansen, S. F. Nielsen, M. D. Thompson, R. A. Reeder, R. M. Izatt and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, 1975, **21**, 874.
14 J. S. Bradshaw, S. T. Jolley and B. A. Jones, *J. Heterocycl. Chem.*, 1980, **17**, 1317.
15 Yu. V. Baskakova, O. V. Yarmolenko, N. I. Shuvalova, G. Z. Tulibaeva and O. N. Efimov, *Russ. J. Electrochem.*, 2006, **42**, 949 (*Elektrokhimiya*, 2006, **42**, 1055).
16 G. Z. Tulibaeva, O. V. Yarmolenko and A. F. Shestakov, *Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1589 (*Izv. Akad. Nauk, Ser. Khim.*, 2009, 1542).
17 G. R. Baymuratova, A. A. Slesarenko, A. V. Yudina and O. V. Yarmolenko, *Russ. Chem. Bull., Int. Ed.*, 2018, **67**, 1648 (*Izv. Akad. Nauk, Ser. Khim.*, 2018, 1648).

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