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Cyclability enhancement and decreasing the irreversible capacity of anodes based on germanium nanowires for lithium-ion batteries

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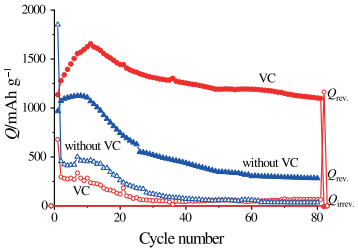
The electrochemical behavior of electrodes based on germanium nanowires in an electrolyte containing 1 M $LiClO_4$ in a propylene carbonate–dimethoxyethane mixture (7 : 3) with 2 wt% vinylene carbonate (VC) was studied. The additive of VC in this electrolyte decreased the irreversible capacity, increased the reversible capacity, and decreased the degradation rate of germanium electrodes in the course of cycling.



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The irreversible capacity, a difference between the charges consumed during charging and returned during discharging, is a key issue in the development of new electrode materials for lithium-ion batteries. The irreversible capacity of anode materials is associated with electrolyte reduction under cathodic polarization and the corresponding formation of a solid electrolyte interface (SEI) on the surface of the anode material.[1] The formation of SEI is necessary for the subsequent reversible insertion of lithium. On the other hand, the irreversible capacity should be as small as possible since it affects the specific characteristics of a lithium-ion battery as a whole: the higher the irreversible capacity, the smaller the energy density of the battery.

It is well known[1] that various anode materials in electrolytes based on propylene carbonate (PC) are characterized by a higher irreversible capacity than that in traditional electrolytes based on ethylene carbonate (EC). This is due to the fact that PC is reduced at less negative potentials than EC, and the SEI formed upon PC reduction has a more defective structure than the SEI formed upon EC reduction. Various electrolyte additives are used to diminish the irreversible capacity of anodes, vinylene carbonate (VC) being most popular. Initially, VC was proposed to improve the SEI on graphite-based anodes; more recently, a beneficial effect of VC on the SEIs on other anode materials including silicon[2–7] and even on cathode materials was found. The detailed mechanism of action of VC on SEI is still a matter of discussion,[8–11] but it was noted that VC was reduced on the anode material before (at less negative potentials) the reduction of PC and EC with the formation of a thin defect-free SEI with high ionic conductivity and good mechanical properties. The effect of VC is comparable to the effect of a polymer electrolyte with a carbonate plasticizer.[12] Only one study on the role of VC in the formation of SEIs on germanium nanowires is documented.[13]

In this work, we were the first to study an electrolyte comprising 1 M $LiClO_4$ in a PC–dimethoxyethane (DME) mixture (7 : 3) with 2 wt% VC on anodes based on germanium nanowires†. Germanium possesses a much higher specific capacity in comparison with graphite (1384 *vs.* 372 mAh g^{-1}), and it can be used as a nanomaterial due to huge volumetric changes upon cycling.

Figure 1 shows the galvanostatic charge–discharge curves of germanium electrodes‡ in the first and second cycles in electrolytes with and without VC.§ The addition of VC to the electrolyte

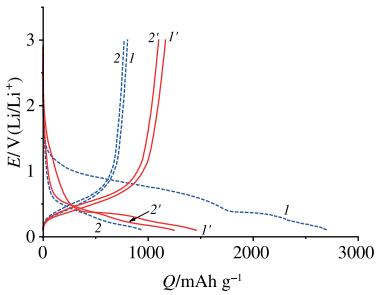

Figure 1 Charge and discharge curves for the (*1*, *1′*) 1st and (*2*, *2′*) 2nd cycles of electrodes based on germanium nanowires in electrolytes (*1*, *2*) without and (*1′*, *2′*) with 2% VC additives.

† Germanium nanowires on indium seeds were synthesized as described previously.[14] The insertion of lithium into such structures was reported,[15] and a battery with a negative electrode based on these structures and a positive electrode based on a ternary oxide (NCA) was described.[16] The amount of germanium on the substrate was about 50 μg cm^{-2}.

‡ Galvanostatic measurements were performed using a multichannel cycler (OJSC Booster, Russia). Three-electrode cells containing a working germanium electrode, an auxiliary lithium electrode, and a lithium reference electrode were assembled in a glove box (CJSC Spectroscopic Systems, Russia).

§ The electrolytes (1 M $LiClO_4$ in the PC–DME (7:3) mixture with and without VC additives) were prepared using commercial battery grade reagents (Sigma-Aldrich). The water content of the electrolytes measured by K. Fischer coulometric titration (Metrohm 917 Coulometer) did not exceed 15 ppm.

considerably changed the shape of the cathodic curve in the first cycle with the disappearance of a long plateau at 1.5–0.45 V; that is, the irreversible capacity of a germanium electrode decreased in the first cycle. The irreversible capacities were about 1900 and 360 mAh g^{-1} in the electrolytes without VC and with the addition of 2% VC, respectively. Moreover, the reversible (anodic) capacity of germanium nanowires in the electrolyte containing VC was higher than that in the electrolyte without the additive.

Figure 2 shows the dynamics of variations in the cathode and anode capacities and the Coulombic efficiency of cycling of germanium nanowires in electrolytes with and without 2% VC additives. In both electrolytes, the capacity increased in the first 10–15 cycles due to the pulverization of germanium particles. This phenomenon is typical of high-capacity anode materials whose unit cells become several times larger upon the insertion of lithium.[17,18]

After the 15th charge–discharge cycle (Figure 2), the specific capacity of germanium nanowires in the electrolyte without additives began to decrease gradually from cycle to cycle, whereas the specific capacity of germanium in the electrolyte containing VC remained nearly unchanged for at least 80 cycles. The germanium nanowires in the electrolyte without VC lost 65% capacity after the first 50 cycles. Previously,[13] the effect of VC added to an electrolyte of 1 M $LiPF_6$ in an EC–dimethyl carbonate mixture was observed for germanium nanowires grown on tin seeds: the stability of the composite increased in the course of cycling, but a decrease in the irreversible capacity in the first cycle was not discussed.

Unambiguously, the electrochemical characteristics of germanium nanowires in the electrolyte containing VC are improved due to the formation of a SEI that affects the lithium ion conductivity and degradation in the course of cycling. This was confirmed by an analysis of the electrochemical impedance spectra of germanium nanowires¶ [Figure 3(*a*)] recorded after the first cathodic polarization when germanium nanowires were completely lithiated and a solid electrolyte film was formed on their surface. The electrochemical impedance spectra were analyzed using an equivalent circuit [Figure 3(*b*)]. The calculated equivalent circuit parameters (Table 1) showed that the resistance of a solid electrolyte film on the surface of germanium nanowires in an electrolyte containing 2% VC was smaller than that in the electrolyte without VC by a factor of 2.6. The rest of the equivalent circuit parameters were nearly the same.

Thus, we found that the addition of VC to a PC-based electrolyte caused a noticeable decrease in the irreversible capacity and an increase in the reversible capacity upon the insertion of lithium into electrodes based on germanium nanowires, which are promising materials for applications in new-generation lithium-ion batteries.

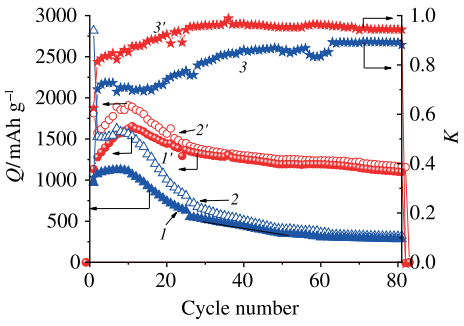

Figure 2 Variations in the (*1*, *1′*) anodic and (*2*, *2′*) cathodic capacities and (*3*, *3′*) the Coulomb efficiency (*K*) of electrodes based on germanium nanowires in electrolytes (*1*–*3*) without and with (*1′*–*3′*) the addition of 2% VC.

¶ Electrochemical impedance spectra were recorded using a P-40X potentiostat with an FRA-24M module (Electrochemical Instruments, Russia) at a potential of 0.2 V (*versus* Li/Li^+) in a frequency range from 0.1 MHz to 0.1 Hz. The voltage amplitude was 10 mV.

Table 1 Parameters of the equivalent circuit of germanium nanowires in the electrolytes.[a]

Parameter	R_s/Ω	C_{SEI}/F	R_{SEI}/Ω	C_{dl}/F	R_{ct}/Ω	W_o/[b] Ω $s^{-0.5}$
Electrolyte without VC	2.1779	4.26×10^{-5}	27.71	4.21×10^{-6}	52.989	250
Electrolyte with 2% VC	4.3336	4.24×10^{-5}	10.85	1.77×10^{-6}	67.828	257

[a] R_s is the electrolyte resistance, R_{SEI} is the SEI resistance, C_{SEI} is the SEI capacitance, R_{ct} is the charge-transfer resistance, CPE is a constant phase element, and W_o is the open Warburg impedance. [b] Calculated from the slopes of the low-frequency sections of the plots of the reactive impedance component *vs*. the root of inverse frequency.

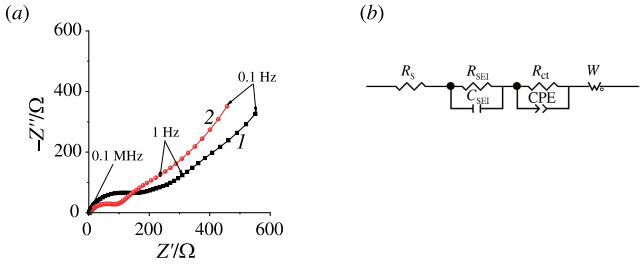

Figure 3 (*a*) Electrochemical impedance spectra of germanium nanowires in electrolytes (*1*) without and (*2*) with an additive of 2% VC; (*b*) an equivalent circuit simulating the impedance spectra.

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References

1 *Lithium-Ion Batteries: Solid-Electrolyte Interphase*, eds. P. B. Balbuena and Y. Wang, Imperial College Press, London, 2004.
2 D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt and U. Heider, *Electrochim. Acta*, 2002, **47**, 1423.
3 S. S. Zhang, *J. Power Sources*, 2006, **162**, 1379.
4 H. Wu, H. Jia, C. Wang, J.-G. Zhang and W. Xu, *Adv. Energy Mater.*, 2021, **11**, 2003092.
5 A. M. Haregewoin, A. S. Wotango and B.-J. Hwang, *Energy Environ. Sci.*, 2016, **9**, 1955.
6 T. Taskovic, L. M. Thompson, A. Eldesoky, M. D. Lumsden and J. R. Dahn, *J. Electrochem. Soc.*, 2021, **168**, 010514.
7 C. C. Nguyen and B. L. Lucht, *J. Electrochem. Soc.*, 2014, **161**, A1933.
8 Y. Wang, S. Nakamura, K. Tasaki and P. B. Balbuena, *J. Am. Chem. Soc.*, 2002, **124**, 4408.
9 Y. Qian, S. Hu, X. Zou, Z. Deng, Y. Xu, Z. Cao, Y. Kang, Y. Deng, Q. Shi, K. Xu and Y. Deng, *Energy Storage Mater.*, 2019, **20**, 208.
10 L. A. Kraynak, J. D. Schneider and A. L. Prieto, *J. Phys. Chem. C*, 2020, **124**, 26083.
11 P. G. Kitz, M. J. Lacey, P. Novák and E. J. Berg, *J. Power Sources*, 2020, **477**, 228567.
12 D. Yu. Voropaeva, S. A. Novikova and A. B. Yaroslavtsev, *Russ. Chem. Rev.*, 2020, **89**, 1132.
13 T. Kennedy, E. Mullane, H. Geaney, M. Osiak, C. O'Dwyer and K. M. Ryan, *Nano Lett.*, 2014, **14**, 716.
14 I. M. Gavrilin, V. A. Smolyaninov, A. A. Dronov, S. A. Gavrilov, A. Yu. Trifonov, T. L. Kulova, A. A. Kuz'mina and A. M. Skundin, *Mendeleev Commun.*, 2018, **28**, 659.
15 I. M. Gavrilin, V. A. Smolyaninov, A. A. Dronov, S. A. Gavrilov, A. Yu. Trifonov, T. L. Kulova, A. A. Kuz'mina and A. M. Skundin, *Russ. J. Electrochem.*, 2018, **54**, 1111 (*Elektrokhimiya*, 2018, **54**, S31).
16 T. L. Kulova, I. M. Gavrilin, Yu. O. Kudryashova and A. M. Skundin, *Mendeleev Commun.*, 2020, **30**, 775.
17 C. Julien, A. Mauger, A. Vijh and K. Zaghib, *Lithium Batteries: Science and Technology*, Springer, 2016.
18 V. S. Bagotsky, A. M. Skundin and Yu. M. Volfkovich, *Electrochemical Power Sources: Batteries, Fuel Cells, and Supercapacitors*, Wiley, 2015.

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