Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 238–239
Mendeleev Communications

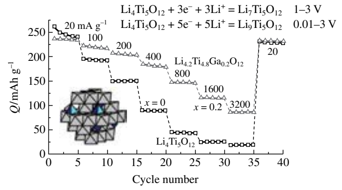
New high-capacity anode materials based on gallium-doped lithium titanate

**Tatiana L. Kulova,[a] Yulia M. Kreshchenova,[b] Anna A. Kuz'mina,[c]
Alexander M. Skundin,[a] Irina A. Stenina[d] and Andrey B. Yaroslavtsev*[d]**

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation*
[b] *Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation*
[c] *National Research University 'MPEI', 111250 Moscow, Russian Federation*
[d] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 954 1279; e-mail: yaroslav@igic.ras.ru*

DOI: 10.1016/j.mencom.2016.05.005

New anode materials based on gallium-doped lithium titanate were obtained. Doping leads to an increase in the capacity of lithium titanate and its cycling stability in an extended potential range from 0.01 to 3 V.



The most widely used anode materials for lithium ion batteries are graphite, silicon, and tin. However, their cycling is extremely unstable, and they rapidly lose their capacity especially at high current densities. Therefore, lithium titanate, which stably works at high current densities up to 20 C (which corresponds to the full charge for 1/20 of an hour), is considered as a promising anode material. The charge–discharge curve of this material represents a plateau at a potential of 1.55 V *vs.* the lithium reference electrode, which appears due to the existence of two lithiated ($Li_7Ti_5O_{12}$) and delithiated ($Li_4Ti_5O_{12}$) phases.[1]

A low change in the cubic cell parameter of this compound (from 8.3595 to 8.3538 Å) determines a high stability of the material during cycling. In the case of the intercalation of three lithium ions per formula unit of lithium titanate, the theoretical capacity is about 175 mAh g^{-1}.[2,3] At the same time, it was shown that the complete reduction of all titanium ions up to the oxidation state +3 is possible, which allows one to increase the theoretical capacity up to 290 mAh g^{-1}.[4,5] However, when the potential is lower than 1 V, the capacity of this material reduces quickly, although there are published data on its stable cycling.[6]

Here, we demonstrate for the first time the high electrochemical capacity and stability during cycling at high current densities of new anode materials based on the gallium-doped lithium titanate $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ ($x = 0.1$ or 0.2).

The lithium titanates $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ ($x = 0$, 0.1 and 0.2) were synthesized using a citrate method. Only the $Li_4Ti_5O_{12}$ reflexes are present on the X-ray diffraction patterns of $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ samples with the substitution degree of 0, 0.1, which indicates that these materials are single-phase. The presence of the Li_2TiO_3 reflexes can be noted for the $Li_{4.2}Ti_{4.8}Ga_{0.2}O_{12}$ materials.

During the study of lithium titanate in an electrochemical cell with a counter electrode of lithium metal, the lithium insertion cathode process corresponds to the charge of lithium titanate, and the lithium extraction anode process corresponds to the discharge of lithium titanate in a lithium ion battery. The charge–discharge curves of lithium titanate and doped lithium titanate in a potential range of 1–3 V present well-defined plateaus at 1.55 V [Figure 1(*a*)]. Coulombic efficiency of cycling reaches 97% for $Li_4Ti_5O_{12}$ already in the second cycle. Discharge capacity decreases with the gallium content, and it is 158, 144, or 141 mAh g^{-1} for $Li_4Ti_5O_{12}$, $Li_{4.1}Ti_{4.9}Ga_{0.1}O_{12}$, or $Li_{4.2}Ti_{4.8}Ga_{0.2}O_{12}$, respectively.

According to Figure 2, doping leads to a decrease in the initial discharge capacity [at a current density of 20 mA g^{-1}, which approximately corresponds to eight hours of discharge

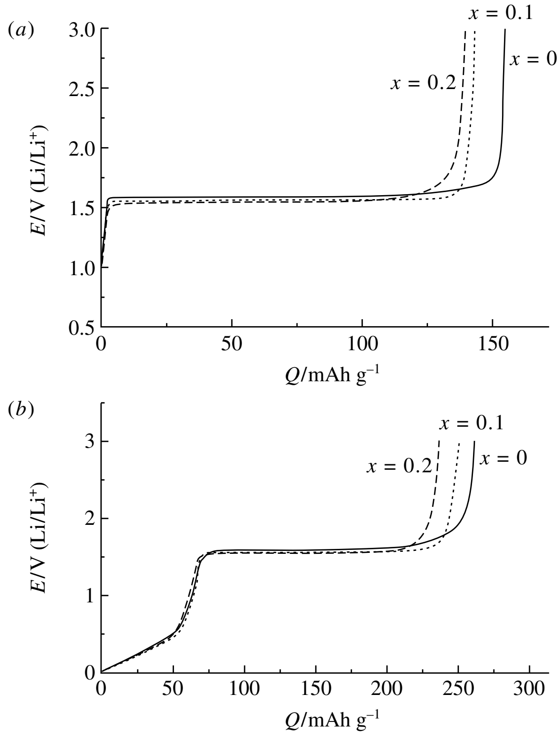


Figure 1 Discharge curves of $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ in the potential ranges of (*a*) 1–3 and (*b*) 0.01–3 V for the second cycle. The current density is 20 mA g^{-1}.

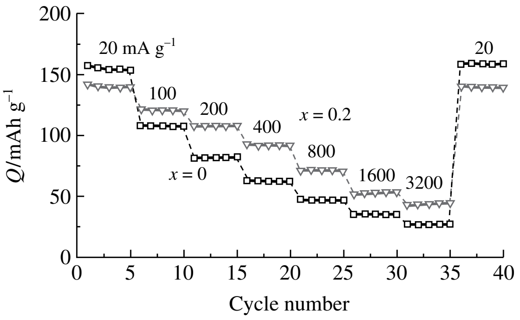


Figure 2 Cycling performance of the $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ lithium titanate samples in a range of 1–3 V at various current densities.

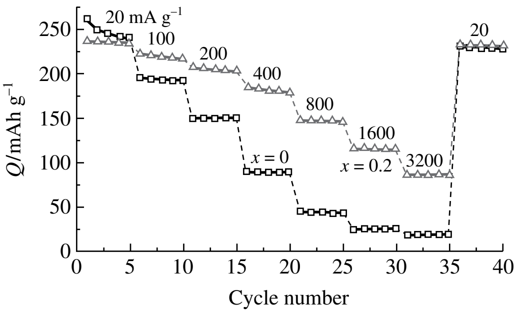


Figure 3 Cycling performance of the $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ lithium titanate samples in a range of 0.01–3 V at various current densities.

(*C*/8)], while at high current densities the discharge capacity of doped samples is higher than the capacity of $Li_4Ti_5O_{12}$. Note that, after returning to low current densities, the discharge capacity of samples is almost the same as the value found in the first cycles (Figure 2). This testifies to the low degradation of samples during cycling.

When the end-potential used for lithium intercalation is decreased to 0.01 V, the discharge capacity of all $Li_{4+x}Ti_{5-x}Ga_xO_{12}$ samples increased to reach 258, 248, and 236 mAh g^{-1} for $x = 0$, 0.1, and 0.2, respectively [Figure 1(*b*)]. At the same time, the plateau at 1.55 V, which corresponds to lithium intercalation in the case of the coexistence of two phases ($Li_{4+x}Ti_{5-x}Ga_xO_{12}$ and $Li_7Ti_{5-x}Ga_xO_{12}$), remained, and the potential gradually changed in a range of 1.5–0.01 V, which reflects the formation of $Li_9Ti_{5-x}Ga_xO_{12}$ solid solutions in $Li_7Ti_{5-x}Ga_xO_{12}$ [Figure 1(*b*)].

As in the potential range of 0.01–3 V, a decrease in the capacity was observed at high current densities (Figure 3). This decrease is the most pronounced in the case of $Li_4Ti_5O_{12}$. At the current density of 800 mA g^{-1}, its capacity is lower than that in a range of 1–3 V, whereas at a current density of $\geqslant 200$ mA g^{-1} the capacity of $Li_{4.2}Ti_{4.8}Ga_{0.2}O_{12}$ in a potential range of 0.01–3 V is two times higher. The capacity of $Li_{4.2}Ti_{4.8}Ga_{0.2}O_{12}$ is higher by a factor of 4.5–5 than that of $Li_4Ti_5O_{12}$ at high current densities (Figure 3). Furthermore, in the case of doped sample, the capacity comes back to its initial value and its decrease does not exceed 0.04% per cycle after returning to low current densities, while in the case of $Li_4Ti_5O_{12}$ the loss is almost an order of magnitude higher. Thus, the use of $Li_{4.2}Ti_{4.8}Ga_{0.2}O_{12}$ in the potential range of 0.01–3 V allows one to perform the charge and discharge of the battery with a capacity of 115 mAh g^{-1} within 6 min.

This work was supported by the Russian Foundation for Basic Research (project no. 14-29-04068 ofi_m).

References

1 A. B. Yaroslavtsev, T. L. Kulova and A. M. Skundin, *Russ. Chem. Rev.*, 2015, **84**, 826.

2 J. Lu, C. Nan, Q. Peng and Y. Li, *J. Power Sources*, 2012, **202**, 246.

3 M. V. Reddy, G. V. Subba Rao and B. V. R. Chowdari, *Chem. Rev.*, 2013, **113**, 5364.

4 L. Aldon, P. Kubiak, M. Womes, J. C. Jumas, J. Oliver-Fourcade, J. L. Tirado, J. I. Corredor and C. Peres Vicente, *Chem. Mater.*, 2004, **16**, 5721.

5 W. Cho, J. Ho Song, M.-S. Park, J.-H. Kim, J.-S. Kim and Y.-J. Kim, *J. Electrochem. Sci. Technol.*, 2010, **1**, 85.

6 J. Shu, *J. Solid State Electrochem.*, 2009, **12**, 1535.

Received: 13th October 2015; Com. 15/4748