Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2024, **34**, 88–89

Mendeleev Communications

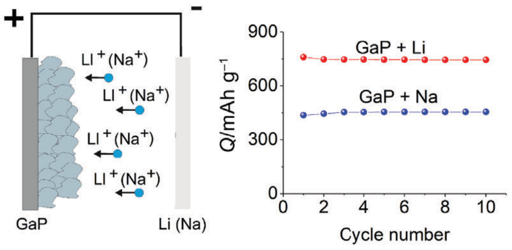
Electrochemical interaction of lithium and sodium with gallium phosphide

Dmitry Yu. Gryzlov, Tatiana L. Kulova, Alsu G. Nugmanova, Alexander M. Skundin* and Yulia O. Kudryashova

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. E-mail: askundin@mail.ru

DOI: 10.1016/j.mencom.2024.01.026

Gallium phosphide (GaP) was synthesized and studied as an anode functional material for lithium-ion and sodium-ion batteries. Electrochemical interaction of GaP with lithium and sodium was compared. The reversible capacity of GaP toward lithium and sodium insertion was found to be about 760 and 465 mAh g^{-1}, respectively.



Keywords: gallium phosphide, lithium-ion battery, sodium-ion battery, interaction with lithium and sodium, reversible capacity.

Metal phosphides are of interest as materials for negative electrodes (anodes) of lithium-ion and sodium-ion batteries. Indeed, their specific capacity exceeds that of graphite and hard carbon,[1–3] and it is comparable with the capacity of germanium-based anode materials.[4,5] By now, the mechanism of reversible interaction of lithium (sodium) with metal (Me) phosphides has been investigated in more or less details, and it is commonly accepted that this interaction occurs *via* two scenario runs:

$$Me_xP + (3 + xy)Li \leftrightarrow Li_3P + xMeLi_y$$

$$Me_xP + (3 + xz)Na \leftrightarrow Na_3P + xMeNa_z \qquad (1)$$

and

$$Me_xP + 3yLi \leftrightarrow yLi_3P + xMe$$

$$Me_xP + 3yNa \leftrightarrow yNa_3P + xMe. \qquad (2)$$

It is likely that the theoretical specific capacity of reversible interaction of a metal phosphide with the alkali metal in the former case is higher than that in the latter. Gallium can form alloys with lithium and sodium. According to phase diagrams,[6–8] the richest alloys of gallium with lithium and sodium correspond to the stoichiometry of $GaLi_2$ and Ga_8Na_5, respectively. In this limiting case, the interaction of gallium with lithium and sodium can be described as follows:

$$GaP + 5Li \leftrightarrow GaLi_2 + Li_3P; \qquad (3)$$

$$8GaP + 29Na \leftrightarrow Ga_8Na_5 + 8Na_3P. \qquad (4)$$

The theoretical specific capacity of GaP upon its interaction with lithium and sodium calculated according Faraday laws accounts to 1330 and 965 mAh g^{-1} for processes (3) and (4), respectively. Therefore, this theoretical capacity notably exceeds the corresponding quantities for reversible insertion of lithium and sodium into carbon (372 mAh g^{-1}).

In this work, we synthesized gallium phosphide by evaporation–condensation of an equiatomic mixture of gallium metal and red phosphorus powder at 650 °C in an oxygen-free atmosphere. A gray powder stable in air was obtained as a product of the synthesis. This product was characterized by XRD.[†] The electrochemical behavior was studied by cyclic voltammetry and galvanostatic cycling.[‡]

Figure 1 shows the XRD pattern of synthesized GaP powder. Peaks related to the cubic phase of GaP (PDF 12-0191 Card) and small peaks of gallium oxide (Ga_2O_3) can be seen very clearly. Peaks at 2θ = 28.4°, 47.2°, 55.8°, and 58.7° correspond to the GaP faces (111), (220), (311), and (222), respectively.

The reversible interaction of gallium phosphide with lithium and sodium was illustrated by cyclic voltamograms (CVs, Figure 2) and galvanostatic charge–discharge curves (Figure 3). Note that

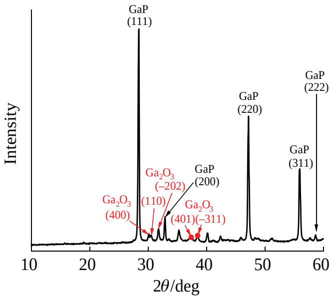


Figure 1 XRD pattern of the synthesized material.

[†] Powder X-ray diffraction of GaP was taken with an Empyrean diffractometer (PANalytical) using Ni-filtered CuKα radiation. The diffractograms were analyzed with the X'pert Highscore Plus software.

[‡] The test electrodes were made of a mixture of 85% GaP, 10% carbon black, and 5% polyvinylidene fluoride applied onto a stainless steel current collector. The electrodes were pressed at 1000 kg cm^{-2} and vacuum dried. Auxiliary and reference electrodes were made of corresponding alkali metals. 1 M $LiPF_6$ in a mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate, and 1 M $NaClO_4$ in a mixture of propylene carbonate with ethylene carbonate were used as electrolytes. The measurements were carried out using a P-208X potentiostat/galvanostat (Elins, Russia). The rate 0.1C corresponded to 133 and 97 mA g^{-1} for lithium and sodium insertion, respectively. The potential scan rate was 0.1 mV s^{-1}.

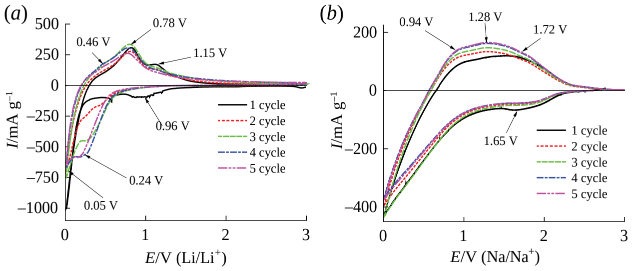


Figure 2 Cyclic voltamograms of GaP at electrochemical interaction with (*a*) lithium and (*b*) sodium for the initial five cycles. The potential scan rate is 0.1 mV s^{-1}.

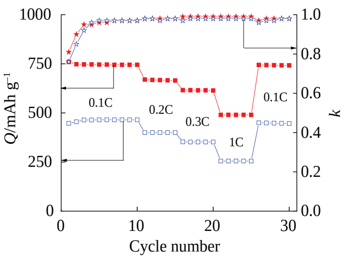


Figure 4 Dependence of (squares) discharge (anode) capacity and (stars) Coulombic efficiency of GaP during electrochemical interaction with (filled) lithium and (empty) sodium.

CVs and galvanostatic curves at the first cycles were notably different from those for the subsequent cycles. This difference was due to the formation of solid electrolyte interface (SEI) films at the GaP surface. Such a difference in the shapes of CVs at the first cycle upon lithium insertion into gallium phosphide was found by Huy *et al.*[9]

Specific cathode and anode peaks on CVs [Figure 2(*a*)] confirmed a complicated process of lithium interaction with GaP. At cathodic polarization, this process included the stages of lithium insertion into GaP ($\mathrm{GaP} + x\mathrm{Li}^+ + xe \rightarrow \mathrm{Li}_x\mathrm{GaP}$, 3–0.65 V), conversion ($\mathrm{Li}_x\mathrm{GaP} + (3 - x)\mathrm{Li}^+ + (3 - x)e \rightarrow \mathrm{Li}_3\mathrm{P} + \mathrm{Ga}$, 0.65–0.24 V), and alloying ($\mathrm{Ga} + y\mathrm{Li}^+ + ye \rightarrow \mathrm{Li}_y\mathrm{Ga}$, 0.24–0.001 V). At anodic polarization, the stages of alloy decomposition ($\mathrm{Li}_y\mathrm{Ga} \rightarrow \mathrm{Ga} + y\mathrm{Li}^+ + ye$, 0.01–0.78 V), deconversion ($\mathrm{Li}_3\mathrm{P} + \mathrm{Ga} \rightarrow \mathrm{Li}_x\mathrm{GaP} + (3 - x)e$, 0.78–1.15 V), and lithium extraction ($\mathrm{Li}_x\mathrm{GaP} \rightarrow \mathrm{GaP} + x\mathrm{Li}^+ + xe$, 1.15–3 V) occurred.

Peculiar plateaus (although less pronounced) corresponding to the above stages can be seen in galvanostatic charge–discharge curves [Figure 3(*a*)], which are consistent with the published data.[9]

Cathode and anode peaks on CVs for reversible interaction of GaP with sodium are expressed less clearly. Nevertheless, it is possible to identify some irreversible cathode peak near 1.65 V related to SEI formation at the GaP surface. Anode peaks near 0.94, 1.28, and 1.72 V can be ascribed to the processes of Na–Ga alloy decomposition, deconversion, and sodium extraction from $\mathrm{Na}_x\mathrm{GaP}$.

At a moderate C-rate (0.1C), the discharge capacity was about 760 and 465 mAh g^{-1} upon interaction with lithium and sodium, respectively. These figures correspond to 57% (lithium) and 48% (sodium) relative to corresponding theoretic values, and they are consistent with the published data.[10,11]

Figure 4 shows the results of GaP cycling at various current densities in lithium- and sodium-containing electrolytes. An increase in the current density led to a natural decrease in the discharge capacity; at a rate of 1C, the discharge capacities of GaP were 490 and 240 mAh g^{-1} when interacting with lithium and sodium, respectively. The Coulombic efficiencies in the first cycle were 81 and 76% for the interaction of GaP with lithium and sodium, respectively. With further cycling, the Coulomb efficiency increased to 98–99%. Degradation of GaP on cycling was 0.14 or 0.18% per cycle in lithium- and sodium-containing electrolytes, respectively. A decrease in degradation during cycling of GaP compared, for example, with GeP is explained by the lower volumetric expansion of gallium. According to Liang *et al.*,[12] the volume expansion of fully lithiated gallium is 160%, which is significantly lower than the volume expansion of silicon and germanium upon lithiation. In addition, the fluidity of the Ga intermediate leads to a reduction in irreversible damage to GaP during cycling.[3]

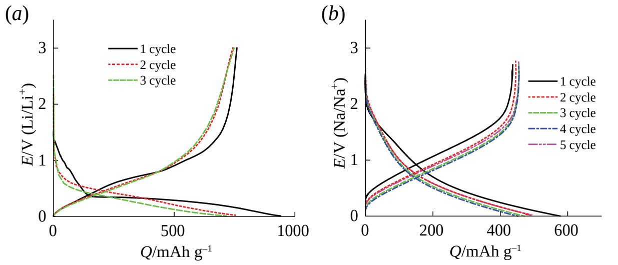


Figure 3 Galvanostatic charge–discharge curves of GaP at electrochemical interaction with (*a*) lithium and (*b*) sodium for the initial cycles. The C-rate is 0.1C.

Thus, gallium phosphide (GaP) synthesized by evaporation–condensation of gallium and red phosphorus is a novel prospect material for lithium-ion and sodium-ion batteries. The discharge capacity of GaP at about 760 or 465 mAh g^{-1} upon interaction with lithium or sodium, respectively, exceeds that of graphite and hard carbon by factors of 1.5 and 2, respectively.

This work was supported by the Russian Science Foundation (project no. 21-13-00160; https://rscf.ru/en/project/21-13-00160/).

References

1 P. U. Nzereogu, A. D. Omah, F. I. Ezema, E. I. Iwuoha and A. C. Nwanya, *Appl. Surf. Sci. Adv.*, 2022, **9**, 100233.
2 W. Zhang, F. Zhang, F. Ming and H. N. Alshareef, *EnergyChem*, 2019, **1**, 100012.
3 W. Zhang, T. Liu, Y. Wang, Y. Liu, J. Nai, L. Zhang, S. Ouwei and X. Tao, *Nano Energy*, 2021, **90**, 106475.
4 T. L. Kulova, I. M. Gavrilin, Yu. O. Kudryashova and A. M. Skundin, *Mendeleev Commun*., 2020, **30**, 775.
5 Yu. O. Kudryashova, I. M. Gavrilin, T. L. Kulova, S. A. Novikova and A. M. Skundin, *Mendeleev Commun*., 2023, **33**, 318.
6 *Diagrammy sostoyaniya dvoinykh metallicheskikh sistem* (*Phase Diagrams of Double Metal Systems*), ed. N. P. Lyakishev, Mashinostroenie, Moscow, 1996–2000 (in Russian).
7 M. Hansen, *Der Aufbau der Zweistofflegierungen*, Springer, Berlin, 1936.
8 R. P. Elliot, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York, 1965.
9 V. P. H. Huy, S. So, I. T. Kim and J. Hur, *Energy Storage Mater*., 2021, **34**, 669.
10 T. Zeng, D. Feng, Q. Liu, S. Ha and R. Zhou, *J. Alloys Compd*., 2021, **883**, 160857.
11 H. Shen, Z. Ma, B. Yang, B. Guo, Y. Lyu, P. Wang, H. Yang, Q. Li, H. Wang, Z. Liu and A. Ni, *J. Power Sources*, 2019, **433**, 126682.
12 W. Liang, L. Hong, H. Yang, F. Fan, Y. Liu, H. Li, J. Li, J. Y. Huang, L.-Q. Chen, T. Zhu and S. Zhang, *Nano Lett*., 2013, **13**, 5212.

Received: 23rd August 2023; Com. 23/7232