

ELECTROCHEMICAL SYNTHESIS OF THE  $\text{TiAl}_{1-x}\text{Li}_x$  PHASE*Kordan V. M., Zhyskovich O. R., Zelinska O. Ya., Pavlyuk V. V.*

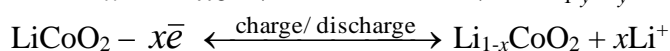
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Intermetallic compounds containing large voids can be used as potential electrode materials in Li-ion batteries. Our previous investigations showed that the size of the voids and the amount of intercalated Li depends on the transition metal. The type of lithiation reaction (inclusion or substitution) and the type of solid solution formed as a result of lithiation depends on the *p*-element.

A sample with the composition  $\text{Ti}_{50}\text{Al}_{50}$  was synthesized by arc melting of the mixture of pure metals with further homogenization annealing in evacuated silica tube at 400 °C for 2 months. The X-ray phase analysis (diffractometer DRON-2.0M,  $\text{FeK}\alpha$  - radiation) confirmed the formation of TiAl (structure type CuAl, space group  $P4/mmm$ ) as a major phase and negligible amount of  $\text{TiAl}_3$  (own structure type, space group  $I4/mmm$ ) as a minor phase. Electrochemical investigation was carried out in the 2-electrode Swagelok-type cell using the powder of the studied alloy as a negative electrode and a powder of  $\text{LiCoO}_2$  (structure type  $\text{NaFeO}_2$ ) as a positive electrode. As electrolyte we used 1M solution of  $\text{Li}[\text{PF}_6]$  in 1:1 ethylenecarbonate / dimethylcarbonate. All electrochemical investigations were carried out in galvanostatic regime (charge at 1.0 mA and discharge at 0.5 mA) over 50 cycles. The electrochemical reactions at the electrodes were the following:



After electrochemical lithiation we observed the increase of lattice parameters for both major TiAl and minor  $\text{TiAl}_3$  phases. We also observed the large amorphization halo and the evidence of formation of new Li-containing binary phases namely  $\text{LiAl}_3$  (structure type  $\text{Cu}_3\text{Au}$ , space group  $Pm\bar{3}m$ ),  $\text{Li}_3\text{Al}_2$  (own structure type, space group  $R\bar{3}m$ ),  $\text{Li}_9\text{Al}_4$  (own structure type, space group  $C12/m1$ ). The lattice parameters for all observed phases are listed in Table. The reason for the increasing of the lattice parameters of the initial phases after electrochemical lithiation is the formation of the solid solutions of substitution  $\text{TiAl}_{1-x}\text{Li}_x$  and  $\text{TiAl}_{3-x}\text{Li}_x$ , where the Al-atoms ( $r_{\text{Al}} = 1.43 \text{ \AA}$ ) are partially substituted by the Li-atoms ( $r_{\text{Li}} = 1.53 \text{ \AA}$ ).

Table. The lattice parameters of observed phases before and after electrochemical lithiation

| Before intercalation of Li  | After intercalation of Li   | $\Delta V/V, \%$ |
|---|---|------------------|
| <p><b>TiAl</b><br/> <math>a = 3.1874(2) \text{ \AA}, c = 3.9568(2) \text{ \AA},</math><br/> <math>V = 40.199(8) \text{ \AA}^3;</math></p>                               | <p><b><math>\text{TiAl}_{1-x}\text{Li}_x</math></b><br/> <math>a = 3.1986(5) \text{ \AA}, c = 3.9629(6) \text{ \AA},</math><br/> <math>V = 40.54(1) \text{ \AA}^3;</math></p>   | 0.85             |
| <p><b><math>\text{TiAl}_3</math> (traces)</b><br/> <math>a = 3.8215(2) \text{ \AA}, c = 8.588(1) \text{ \AA},</math><br/> <math>V = 125.42(2) \text{ \AA}^3;</math></p> | <p><b><math>\text{TiAl}_{3-x}\text{Li}_x</math> (traces)</b><br/> <math>a = 3.8375(3) \text{ \AA}, c = 8.607(1) \text{ \AA},</math><br/> <math>V = 126.76(3) \text{ \AA}^3;</math></p>  | 1.07             |
|   | <p><b><math>\text{LiAl}_3</math> (traces)</b><br/> <math>a = 4.0101(3) \text{ \AA}, V = 64.48(2) \text{ \AA}^3;</math></p>  |                  |
|   | <p><b><math>\text{Li}_3\text{Al}_2</math> (traces)</b><br/> <math>a = 4.5085(3) \text{ \AA}, c = 14.171(4) \text{ \AA}, V =</math><br/> <math>249.46(6) \text{ \AA}^3;</math></p>   |                  |
|   | <p><b><math>\text{Li}_9\text{Al}_4</math> (traces)</b><br/> <math>a = 18.86(3) \text{ \AA}, b = 4.500(5) \text{ \AA}, c = 5.416(3) \text{ \AA},</math><br/> <math>\beta = 105.3(1)^\circ, V = 443.4(6) \text{ \AA}^3</math></p> |                  |