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Li-Zn-{Al, Sn} ZINTL PHASE ALLOYS FOR THE ANODE MATERIALS OF LITHIUM BATTERIES

G. Dmytriv [1], V. Pavlyuk [1], I. Tarasiuk [1], H. Pauly [2], H. Ehrenberg [2], B. Marciniak [3], W. Prochwicz [3], G. Schroeder [4]

[1] *Ivan Franko Lviv National University,*
Kyryla and Mefodia Str., 6, 79005 Lviv, Ukraine

[2] *Materials Science, Darmstadt University of Technology,*
Petersenstr., 23, D-64287 Darmstadt, Germany

[3] *Institute of Chemistry and Environment Protection, Jan Dlugosz University,*
Armii Krajowej Str., 13/15, 42200 Częstochowa, Poland

[4] *Uniwersytet im. A. Mickiewicza,*
Grunwaldzka Str., 6, 60780 Poznań, Poland

Alloys from homogeneity ranges of solid solution $LiZn_xAl_{1-x}$ ($x = 0–1$) and ternary compound $Li_{2.5-1.5}Zn_{0.5-1.5}Sn$ was investigated as anode materials of lithium batteries. All tested phases crystallized in the Zintl phase NaTl structure (space group $Fd\bar{3}m$). Current sources with these anodes in dependence of cathode materials and composition of anode material characterized by voltage 1.5–3.12 V and energy density 60–240 W h/kg.

Key words: Zintl phase, anode materials, lithium batteries.

Lithium ion rechargeable batteries are used as the power supply of cellular phones and several other portable electrical devices at present, and demand appears to increase exponentially. The concern about energy sources in the near future, either for electric vehicles or for large-scale batteries for electricity power storage, has made lithium ion rechargeable battery development into a growth area, which has gained high momentum for its research activities. There are three directions of current research of materials for lithium batteries: anode materials, electrolytes, and cathode materials [1].

In old models of lithium batteries pure lithium was used as anode material: $Li\text{-}SOCl_2$, $Li\text{-}MnO_2$, $Li\text{-}TiS_2$ and other systems [2, 3]. Carbon matrix with distributed inside lithium is used as the anode-active material in modern lithium ion batteries. In both this case problem of chemical activity of pure lithium exist. This problem can be solving by using lithium alloys which having better technical and energetic parameters.

The main objective of presented investigations is to design of advanced lithium alloys that are attractive construction materials for anodes in both disposable (primary) and rechargeable (secondary) batteries due to its high electrochemical potential combined with a low equivalent mass. The great roles among such alloys play NaTl-type Zintl phases, for example LiAl Zintl phase that was the first commercial product as an anode material [4]. The search of new materials is impossible without the investigation of the phase diagrams, crystal structure of the compounds and their properties.

Alloys for the anode materials was prepared from the pure metals (content of main element not less than 99.99 at. % except lithium, content of lithium – 99.8 at. %). Preparation of alloys was carried out in arc furnace in argon atmosphere at pressure $1.01 \cdot 10^5$ Pa. Alloys was kept in purified indifferent oil after melting.

For the testing of alloys powder patterns was used. X-ray diffraction patterns were collected on a STOE STADI P powder diffractometer ($MoK_{\alpha 1}$ radiation, 0.02° step of scanning, 8 sec/step for the 2θ range 8–50°) or DRON-2.0 powder diffractometer ($FeK_{\alpha 1}$ radiation, 2°/min speed of scanning for the 2θ range 20–90°). The unit cell parameters were refined using the program LATCON [5]. The software package Fullprof was used for Rietveld refinements [6].

Electrochemical investigations was carried out in the real button-types current sources with electrode square 1.65 sm^2 and volume 0.66 sm^3. Lithium contained alloys was processed for obtaining form of anode place in current sources or powdered with next pressing in the mold. Cathode materials (metal oxides: MnO_2, Ag_2O, V_2O_5, MoO_3, PbO_2, CuO; sulfides: TiS_2, FeS_2, FeS and conducting polymer polyacetylene (PAC)) were powdered also. Inorganic salt $LiClO_4$ 1 M dissolved in the organic liquid solvent γ-butyrolactone (BL) was used as electrolyte.

For anode materials in the real button types current sources was used lithium alloys with composition from homogeneity range of continuous solid solution $LiZn_xAl_{1-x}$ (x = 0–1) and ternary compound $Li_{2.5-1.5}Zn_{0.5-1.5}Sn$. Both this phases crystallized in Zintl phase structure type NaTl (space group $Fd\bar{3}m$) [7]. Homogeneity ranges of solid solutions $LiZn_xAl_{1-x}$ (x = 0–1) and ternary compound $Li_{2.5-1.5}Zn_{0.5-1.5}Sn$ are presented in the Table 1.

Table 1

Lattice parameters and composition of the alloys homogeneity ranges of solid solutions $LiZn_xAl_{1-x}$ and ternary compound $Li_{2.5-1.5}Zn_{0.5-1.5}Sn$

$LiZn_xAl_{1-x}$			$Li_{2.5-1.5}Zn_{0.5-1.5}Sn$		
Composition	a, Å	Reference	Composition	a, Å	Reference
LiZn	6.221	[8]	$Li_{2.5}Zn_{0.5}Sn$	6.307(3)	[11]
$LiZn_{0.9}Al_{0.1}$	6.2240(1)	[9]	Li_2ZnSn	6.376(3)	[11]
$LiZn_{0.8}Al_{0.2}$	6.2470(1)	[9]	$Li_{1.5}Zn_{1.5}Sn$	6.449(5)	[11]
$LiZn_{0.7}Al_{0.3}$	6.2592(1)	[9]			
$LiZn_{0.6}Al_{0.4}$	6.2697(1)	[9]			
$LiZn_{0.5}Al_{0.5}$	6.2819(1)	[9]			
$LiZn_{0.4}Al_{0.6}$	6.2987(1)	[9]			
$LiZn_{0.3}Al_{0.7}$	6.3102(1)	[9]			
$LiZn_{0.2}Al_{0.8}$	6.3347(1)	[9]			
LiAl	6.360	[10]			

Results of testing of alloy Li_2ZnAl by crystal structure refinement was presented as an example on Fig. 1.

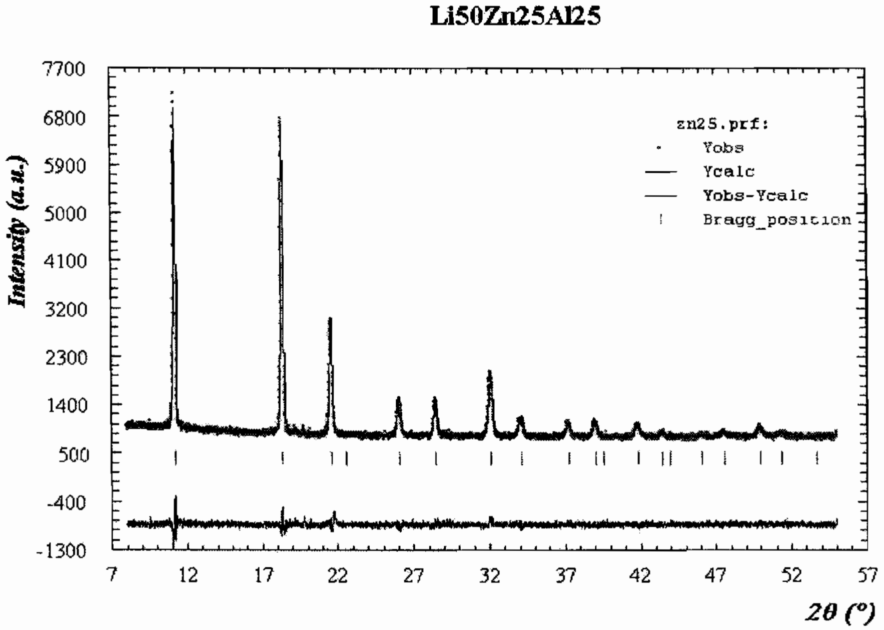

Fig. 1. Observed and calculated X-ray powder diffraction patterns of Li_2ZnAl together with their difference curve

Electrochemical characteristics of batteries with $LiZn_xAl_{1-x}$ anode and different cathodes with organic electrolyte liquids ($LiClO_4$ 1 M dissolved in the γ-butyrolactone (BL)) are presented in the Table 2.

Table 2

Voltage and energy density for the investigated electrochemical systems

System	Voltage (E), [V]	Energy density (W) [W h/kg]
$LiZn_xAl_{1-x}$–MnO_2	2.80–2.27	180–110
$LiZn_xAl_{1-x}$–TiS_2	2.50–1.90	130–100
$LiZn_xAl_{1-x}$–Ag_2O	3.04–2.21	160–100
$LiZn_xAl_{1-x}$–FeS_2	2.00–1.70	110–90
$LiZn_xAl_{1-x}$–(PAC)	3.12–2.42	240–180
$LiZn_xAl_{1-x}$–V_2O_5	2.80–2.30	190–140
$LiZn_xAl_{1-x}$–MoO_3	2.50–1.80	140–110
$Li_{2.5-1.5}Zn_{0.5-1.5}Sn$ –PbO_2	2.82–2.05	105–80
$Li_{2.5-1.5}Zn_{0.5-1.5}Sn$–FeS	1.75–1.50	90–60
$Li_{2.5-1.5}Zn_{0.5-1.5}Sn$–CuO	2.10–1.80	110–90

Discharge curves for some investigated electrochemical systems presented on the Figs. 2–5.

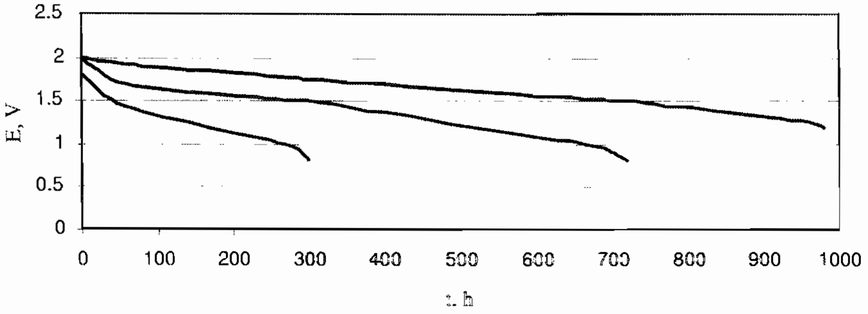

Fig. 2. Discharge curve for the $LiZn_xAl_{1-x}$–MnO_2 system

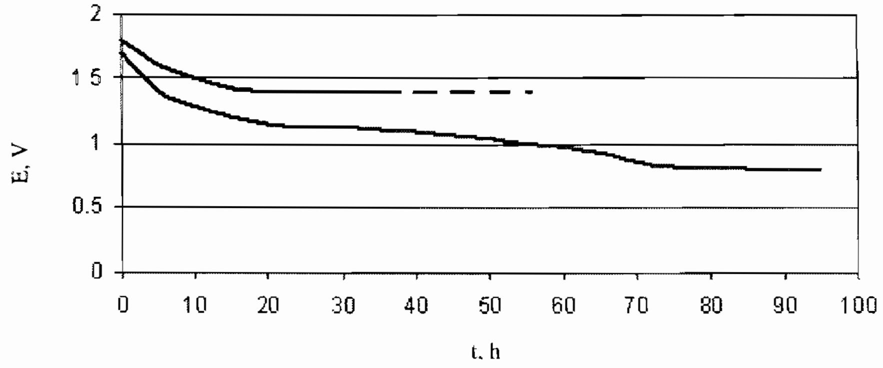

Fig. 3. Discharge curve for the $LiZn_xAl_{1-x}$–Ag_2O system

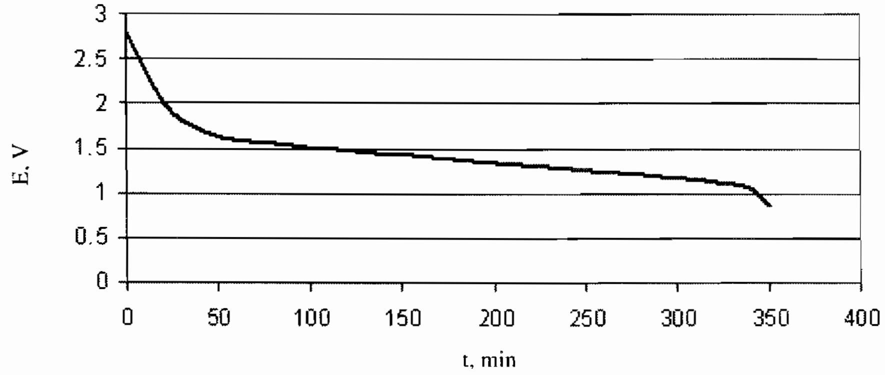

Fig. 4. Discharge curve for the $LiZn_xAl_{1-x}$–PAC system

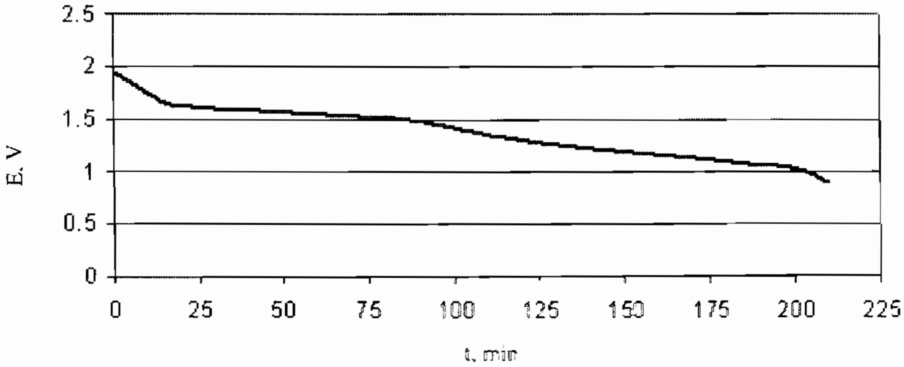

Fig. 5. Discharge curve for the $\mathrm{LiZn}_x\mathrm{Al}_{1-x}$–$\mathrm{Ni_2O_3}$ system

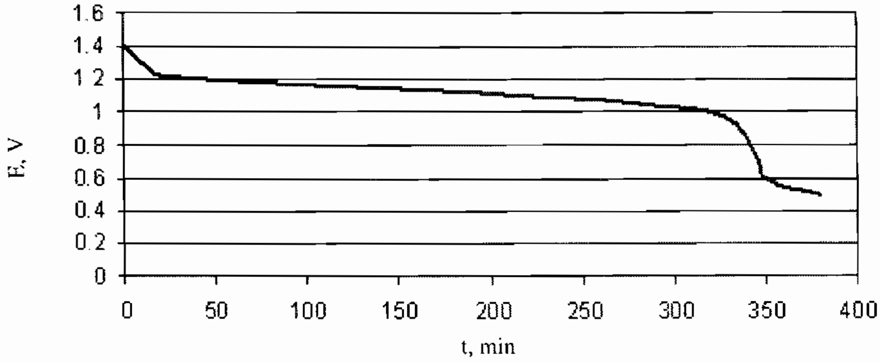

Fig. 6. Discharge curve for the $\mathrm{LiZn}_x\mathrm{Sn}_{1-x}$–HgO system

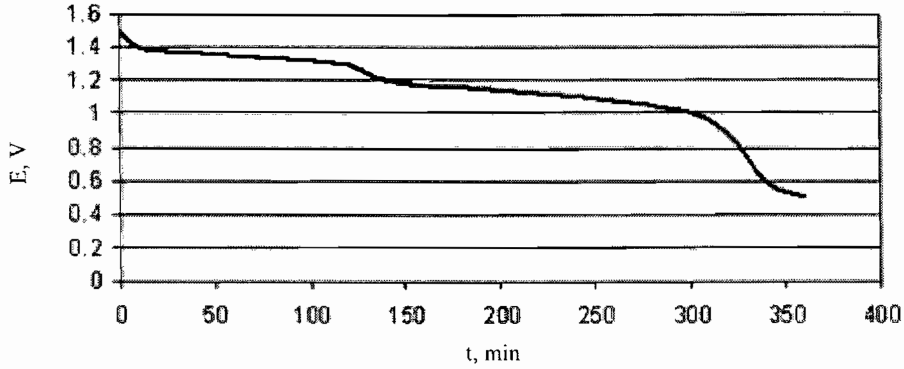

Fig. 7. Discharge curve for the $\mathrm{LiZn}_x\mathrm{Sn}_{1-x}$–$\mathrm{Ag_2O}$ system

Nominal voltage of current sources on the base of the $LiZn_xAl_{1-x}$ (x = 0–1) phases increasing with increasing of Al content independently of cathode materials. Therefore energy density is close to the classic LiAl anode and in some case is higher. It's can be explained by higher stability of the Zn-contained ternary phases in organic liquid electrolyte and lower ability to dendrite formation. Current sources with $Li_{2.5-1.5}Zn_{0.5-1.5}Sn$ anode material characterized by lower energy density but stability of these anode materials also is good.

Acknowelegment

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СПЛАВИ ФАЗ ЦИНТЛЯ СИСТЕМ Li-Zn-{Al, Sn} ДЛЯ АНОДНИХ МАТЕРІАЛІВ ЛІТІЄВИХ БАТАРЕЙ

Г. Дмитрів [1], В. Павлюк [1], І. Тарасюк [1], Г. Паулі [2], Г. Еренберг [2],
Б. Марціняк [3], В. Прохвіч [3], Г. Шредер [4]

[1] Львівський національний університет імені Івана Франка,
вул. Кирила і Мефодія, 6, 79005 Львів, Україна

[2] Інститут матеріалознавства, Технічний університет м. Дармштадт,
Петерсенштрассе, 23, D-64287 Дармштадт, Німеччина

[3] Інститут хімії і захисту довкілля, Університет Яна Длугоша,
вул. Армії Крайової, 13/15, 42200 Ченстохова, Польща

[4] Університет імені Адама Міцкевича,
вул. Грюнвальдська, 6, 60780 Познань, Польща

Сплави з області гомогенності твердого розчину $LiZn_xAl_{1-x}$ ($x = 0–1$) та тернарної сполуки $Li_{2.5-1.5}Zn_{0.5-1.5}Sn$ досліджували як анодні матеріали літієвих батарей. Усі тестовані фази кристалізуються зі структурою фаз Цинтля, структурний тип NaTl (просторова група $Fd\bar{3}m$). Хімічні джерела струму з вказаними анодними матеріалами характеризуються напругою 1,5–3,12 В та питомою енергією 60–240 Вт год/кг залежно від матеріалу катоду та складу матеріалу аноду.

Ключові слова: фази Цинтля, анодні матеріали, літієві батареї.

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