

K₂Ti₆O₁₃/carbon core-shell nanorods as superior anode material for high-rate potassium ion batteries

Cheng Liu ^a, Huili Wang ^a, Shiyu Zhang ^a, Muyao Han ^a, Yu Cao ^a, Shuo Liu ^a, Zhanxu Yang ^{*b} Aibing Chen ^{*c} and Jie Sun ^{*a,d}

^a Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. E-mail: jies@tju.edu.cn

^b College of Chemistry, Chemical Engineering and Environment Engineering, Liaoning Shihua University, Fushun, Liaoning 113001, China. E-mail: zhanxuy@126.com; yangzhanxu@lnpu.edu.cn

^c College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, 70 Yuhua Road, Shijiazhuang 050018, China. E-mail: chen_ab@163.com

^d State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

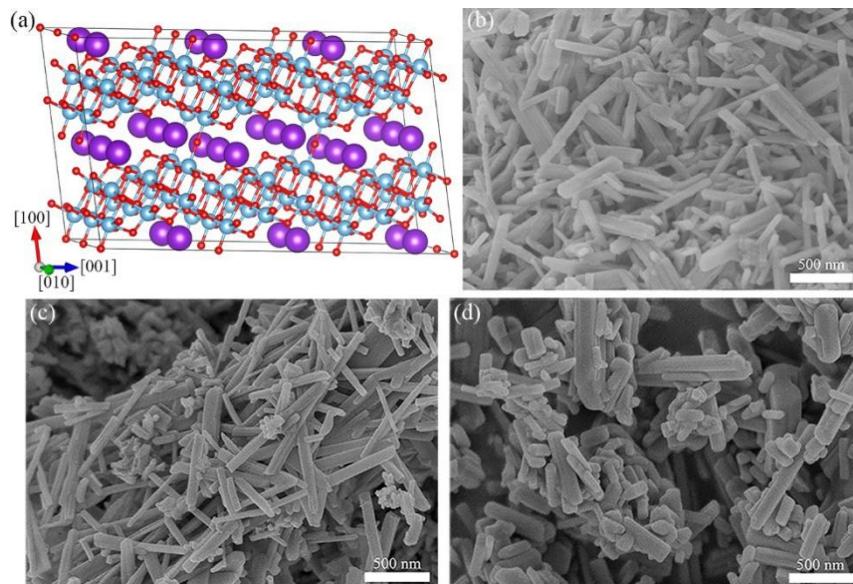


Fig.S1 (a) Ball and stick model of the crystal structure of the K₂Ti₆O₁₃ with the space group C2/m ($a=15.82428\text{ \AA}$, $b=3.82021\text{ \AA}$, $c=9.23647\text{ \AA}$); SEM images of as-prepared samples: (b) K₂Ti₆O₁₃; (c) KTO/C-600 and (d) KTO/C-800.

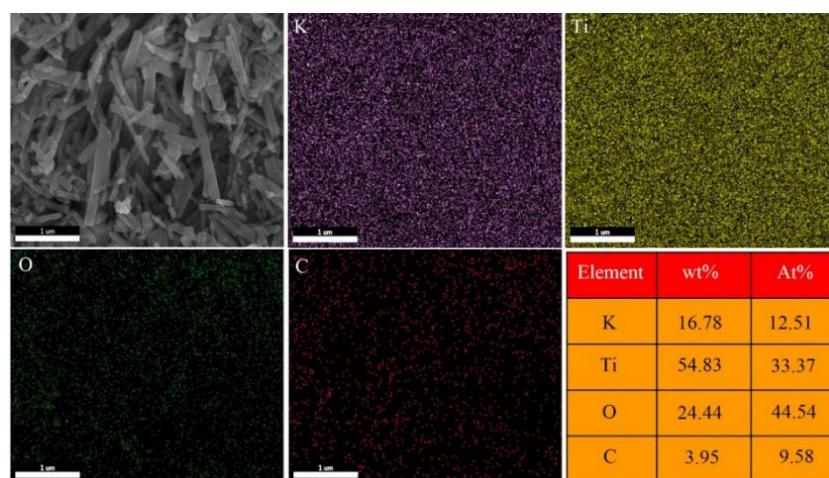


Fig.S2 EDX mapping of KTO/C-700

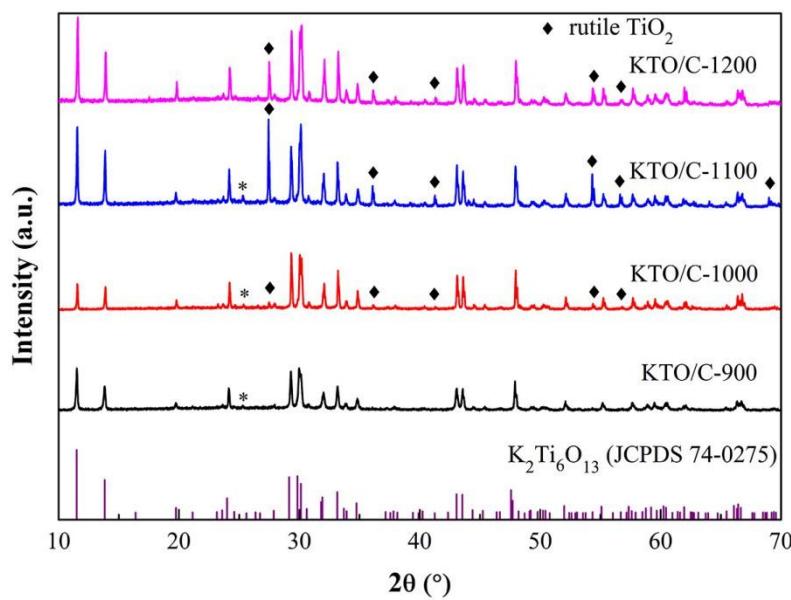


Fig.S3 XRD patterns of the KTO/C-900, KTO/C-1000, KTO/C-1100 and KTO/C-1200

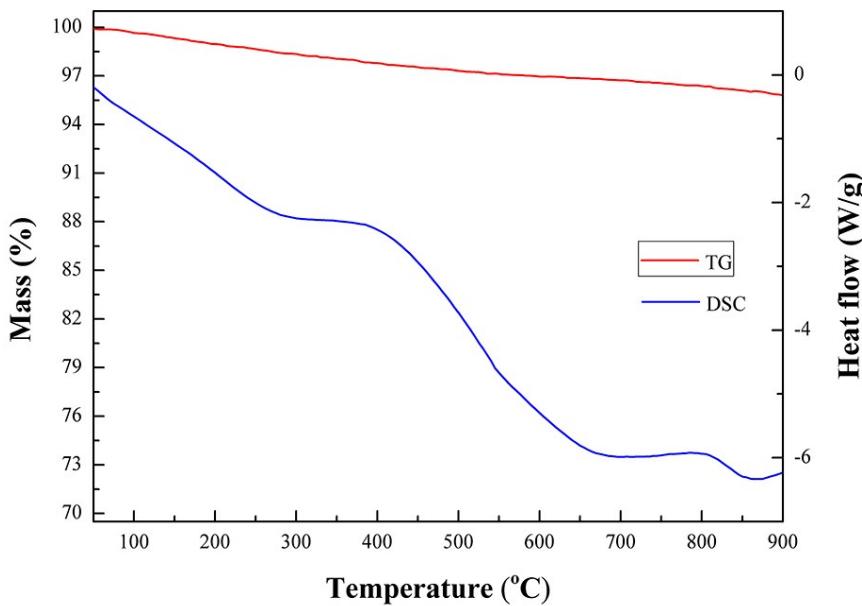


Fig.S4 TGA/DSC of KTO/C precursor at a rate of 10 °C min⁻¹ in N₂

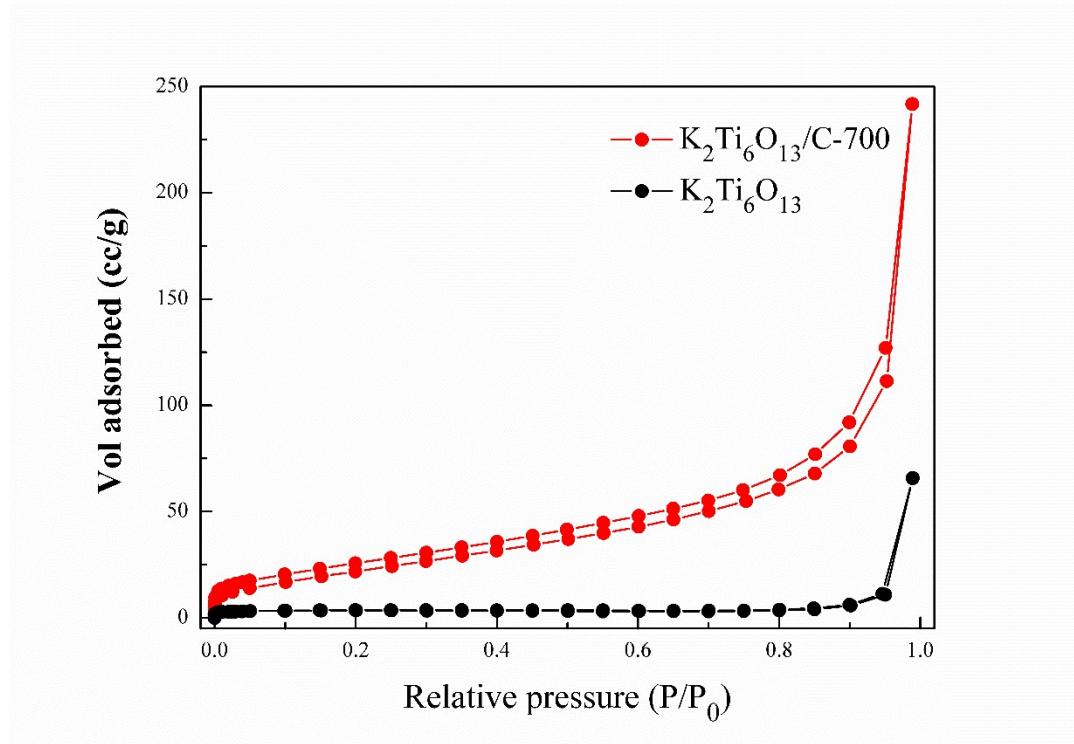


Fig.S5 Adsorption-desorption isotherms of $\text{K}_2\text{Ti}_6\text{O}_{13}$ and $\text{K}_2\text{Ti}_6\text{O}_{13}/\text{C}-700$

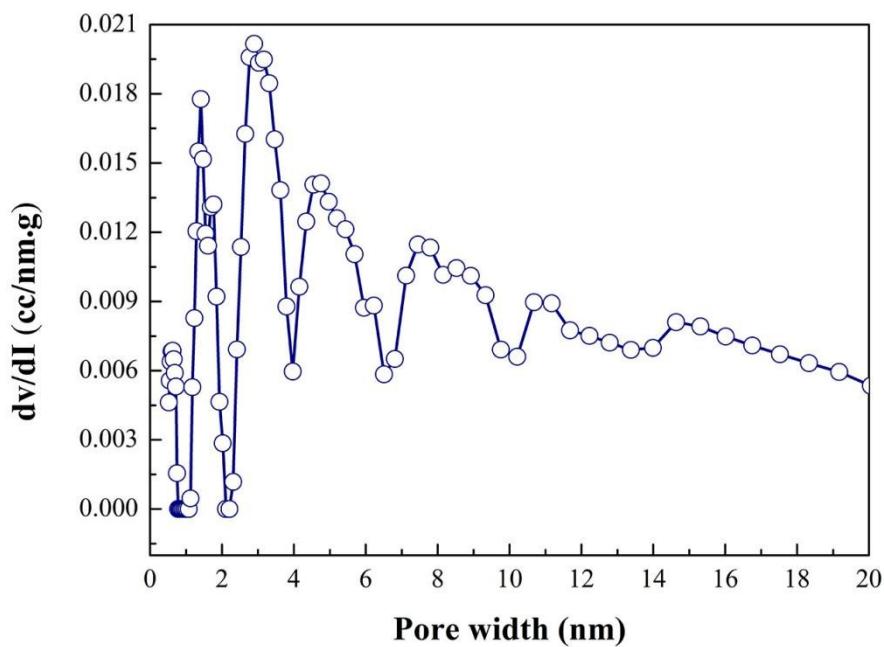


Fig.S6 Pore size distributions of KTO/C-700

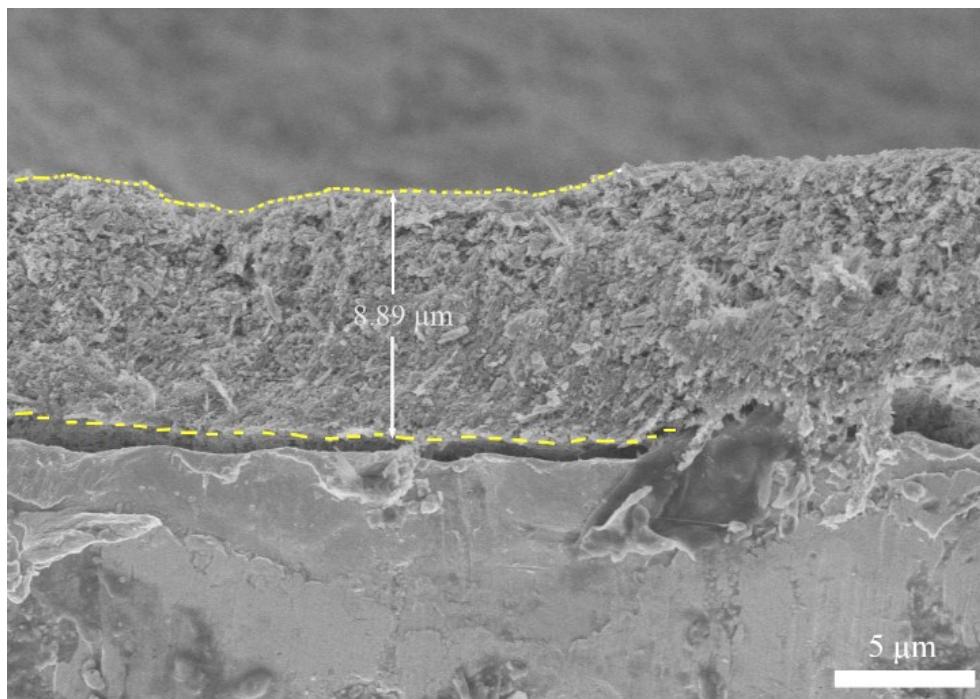


Fig.S7 SEM image of cross-section of electrode for $\text{K}_2\text{Ti}_6\text{O}_{13}/\text{C-700}$

The mass loading of the active materials were about 1.1 mg cm^{-2} . As shown in Fig.S5, a typical electrode thickness was about $8.89 \mu\text{m}$. Thus, the density of the electrode was about 1.77 g cm^{-3} (based on the total mass including active material, super-p carbon and PVDF, except for copper collector). In order to precisely characterize the compaction density of the as-prepared products themselves, the obtained powders were pressed into green bodies (Fig.S6) under 10 MPa pressure by using a manually tablet machine (769YP-15A, Tianjin KeQi High & New Technology Corporation, Tianjin, China). The obtained values are shown in the table S1.

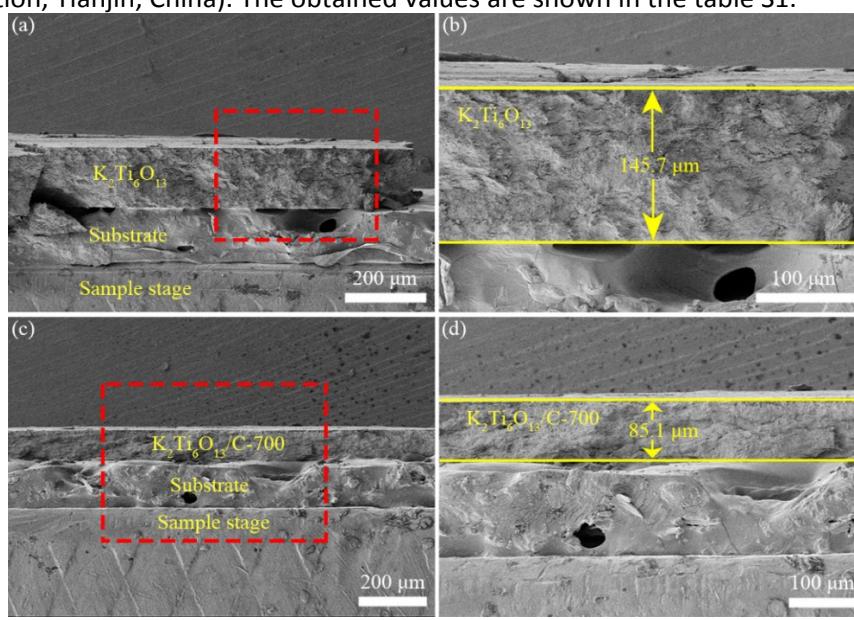


Fig.S8 SEM images of cross-sections of green bodies of (a, b) $\text{K}_2\text{Ti}_6\text{O}_{13}$ and (c, d) $\text{K}_2\text{Ti}_6\text{O}_{13}/\text{C-700}$ with a manually tablet machine (769YP-15A, Tianjin KeQi High & New Technology Corporation, Tianjin, China) under about 10 MPa pressure.

Table S1. Compacted density of the several common anode materials

Morphology	Synthesis method	Compacted density (g cm ⁻³)	Pressure (MPa)	Application	Ref.
Sulfur and nitrogen dual-doped graphene	Chemical vapor deposition	0.4	10	LIBs	[1]
Reduced graphene oxide	Solvent evaporation method	1.3	15	Supercapacitors	[2]
SiO _x @Fe ₃ O ₄ @FLG	Ball milling	1.86	16	LIBs	[3]
Si@SiO ₂	High pressure and ball milling	1.11	17.6	LIBs	[4]
Li ₄ Ti ₅ O ₁₂	Pyrolysis	1.7	-	LIBs	[5]
Expanded graphite	-	1.68	7	Fuel cells	[6]
Carbon nanotubes	-	0.58	0.3-0.4	-	[7]
Carbon nanowires	-	0.52	0.3-0.4	-	[7]
K ₂ Ti ₆ O ₁₃	hydrothermal process	1.91	10	PIBs	This work
K ₂ Ti ₆ O ₁₃ /C	hydrothermal process	1.88	10	PIBs	This work

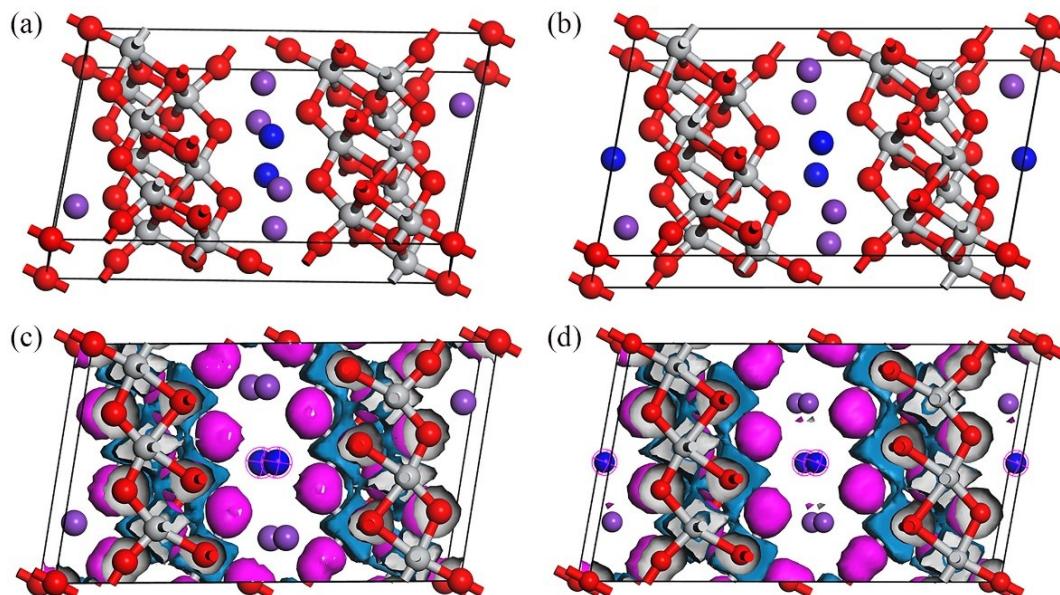
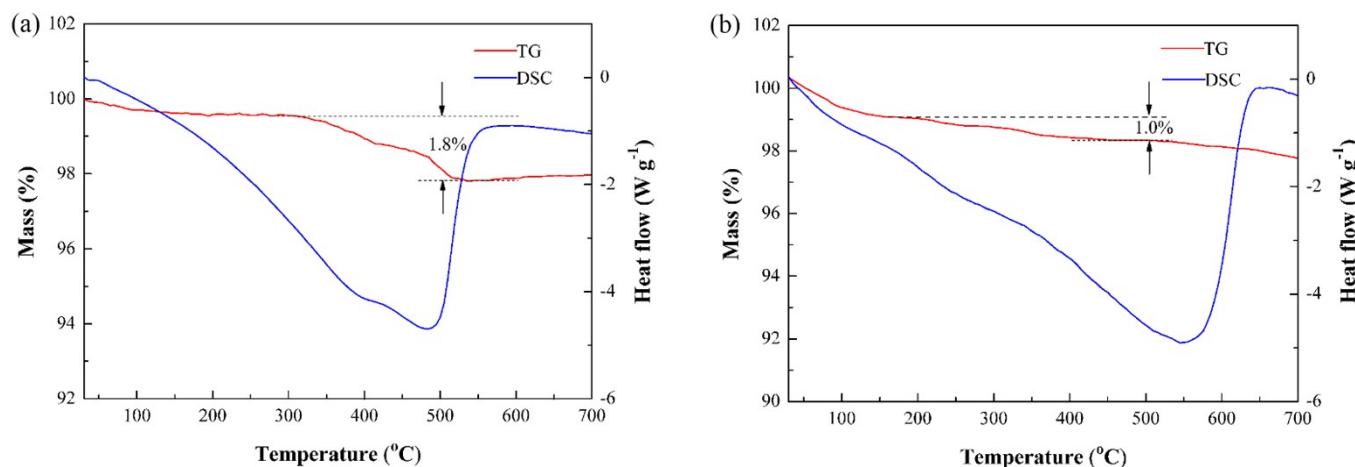


Fig.S9 DFT predicted crystal structures of $\text{K}_{2+x}\text{Ti}_6\text{O}_{13}$. (a) $\text{K}_{2+0.5}\text{Ti}_6\text{O}_{13}$, (b) $\text{K}_{2+1}\text{Ti}_6\text{O}_{13}$ and (c,d) the corresponding electron density difference plots.

Table S2 Lattice parameters of $K_{2+x}Ti_6O_{13}$ collected at various potassium compositions

	<i>a</i>	<i>b</i>	<i>c</i>	β	Cell vol	<i>x</i> in $K_{2+x}Ti_6O_{13}$
original	17.099	3.727	9.686	100.407	607.068	0
Sample A	16.730	4.012	9.581	99.629	633.985	0.5
Sample B	16.470	4.035	9.755	100.549	637.374	1

**Fig.S10 TGA/DSC of (a) KTO/C-700 and (b) KTO/C-800 at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in Air****Table S3 Nyquist Analysis of $K_2Ti_6O_{13}$, KTO/C-600, KTO/C-700 and KTO/C-800 anodes before cycling**

Sample	R_s (Ω)	R_{ct} (Ω)
$K_2Ti_6O_{13}$	2.90	16877
KTO/C-600	2.68	9987
KTO/C-700	2.13	3078
KTO/C-800	3.79	8487

Refer

- [1] X. Ma, G. Ning, Y. Sun, Y. Pu and J. Gao, *Carbon*, **2014**, *79*, 310-320.
- [2] X. Zhang, D. V. Raj, X. Zhou, Z. Liu, *J. Power Sources*, **2018**, *382*, 95-100.
- [3] C. Liao and S. Wu. *Chem. Eng. J.*, **2019**, *355*, 805-814.
- [4] D. Lin, Z. Lu, P.C. Hsu, H. R. Lee, N. Liu, J. Zhao, H. Wang, C. Liu and Y. Cui, *Energy Environ. Sci.*, **2015**, *8*, 2371-2376.
- [5] A. Jaiswal, C. R. Horne, A. Chang, W. Zhang, W. Kong, E. Wang, T. Chen and M. M. Doeff, *J. Electrochem. Soc.* **2009**, *156*, A1041-A1046.
- [6] S.I. Heo, K. S. Oh, J. C. Yun, S. H. Jung, Y. C. Yang and K. S. Han, *J. Power Sources*, **2007**, *171*, 396-403.
- [7] I.V. Zolotukhin, I. M. Golev, A. E. Markova, S.N. Blinov, D. A. Grishin and E. G. Rakov, *Tech. Phys. Lett.*, **2005**, *31*, 159-160.