

Nano-Ionics与锂离子电池

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PS Notional Concept Vehicle. SOURCE: Courtesy ons International Corporation.

g technologies in the development of the combat hybrid power gies to be addressed include permanent magnet technology for gh-temperature, wide band gap materials. Other such FIGURE 1-2 One vers of George Frazier, Scia

> Address the key is system componen hub motors, Li-ior



Power Source Weight for Equal Perf. (Ib)

24

Time



Boot'

Mini Soldier Tectical Redio*

Solar Cell (Fuel[®]

Low Power Processo and Situational Awareness*

* Coupled with Hybrid Power I Power Menagement System







iony回收约700万组 管记本锂离子电池



Solid State Ionics ◆主要研究对象:离子导体(Ionic conductor) 或固体电解质 (Solid State Electrolyte),其电荷载流子是离子, 而非电子。 ☆发展到快离子导体(Superionic) conductor 或Fast ionic conductor), 它们的 离子电导率很高。 ✤拓展到混合离子导体(Mixed) Conductors),其电荷载流子不仅是离

从Solid State Ionics

To Nano-Ionics





1913年Tubandt发现AgI在147C从 相转变到 相,电导率增加3个数量级以上,达

表6.6 Agl以及CuBr的超空温度和填空值(AS, AS_)

	a and a second		· · · · ·	·		
化全场] 分别与二元		čn <u>j - 1</u>				an Thinks
	11_3		Agl	_ 419		14.5 - =
1	12.6	CuBr	66	4 -	9.0	
20 (1976))		۲M (O.Keef	e et al.	Philos.	Mag 3

离子形成bcc晶格,

- 个Ag离子随机分布在
- 2个位置上:
- b(八面体)
- 2d(四面体)
- 4h(三角双锥) 吉构是准熔态



甲子衍射表明: 2个Ag离子位于四面体位(12d), 向八面体位(6b)延伸



FIG. 9. Crystal structure of a-AgI according to Wright and Fender The figure gives the positons and r.m.s. displacements of the nuclei at 200 °C. Systems with $D \ge 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

simple monoatomic \propto -Ag I hydrogen in







































Doubled energy density in 10 years



Evolution of energy for different battery technologies:



J. Moler Nokla Mobile Phones, Fort Lauderdale, FB,March 2000.

Nano-Ionics?





Nanosized Li-Sn grains dispersed in amorphous Li₂O in discharged nano-SnO anode for Li ion batteries



The influence of particle size, content of CB, voltage limitation on the cyclic performance of Si-based anodes for secondary lithium batteries





SAED patterns of Si nanoparticles at different Li-doping levels



Original Nano-Si

Heavy Li-doped

Partly Li-extraction

Nano-SnSb on hard carbon spheres





Morphology of 30wt% nano-SnSb alloy on hard carbon after Li ions insertion and extraction



OKV XI. BAK





Li ions extraction



Microstructure of HCS coated by nanosized SnSb alloy









Perfect Spherical Morphology, Controllable Monodispersed Particle Size and Smooth Surface



HCS的高分辨透射电镜照片

- 典型的无定形碳材 料
- 由单碳层堆积而成
 分布着1 nm以下的 微孔





The second second second

2nm



重要结论

在深嵌锂态观察到管内出现 了大量新相的晶格条纹,在 脱锂态这些条纹消失。根据 条纹间距机步认为在管内壁 形成了锂的高压相。这对多 孔炭材料的嵌锂机理的研究 有重要意义。

FIG. 1. Energetics of diffusion pathways for Li to move through a (a) (5, 5) metallic; and (c) (8, 0) semiconducting nanotube. Contour plots of the resulting charge difference distribution for a Li atom absorbed on (5, 5) and (8, 0) nanotubes are shown in (b) and (d), respectively. The positions of the C(Li) atoms are indicated by the filled (open) circles, respectively.

FIG. 2. Structure of the topological defects displaying different *n*-membered rings. The diffusion barriers through these rings and the corresponding formation energies are given in Table I.

TABLE I. Diffusion barrier ΔE and formation energy E_F for each of the topological defects shown in Fig. 2. The formation energy is measured with respect to the hexagon.

	ΔE (eV)	E_F (eV)	
Hexagon	13.5	0.0	
Heptagon	7.5	3.5	
Octagon	3.0	6.2	
Enneagon	0.5	9.5	

FIG. 3. Estimated residence time τ as a function of nanotube length L at T = 300 K for Li atoms in either the nanotube interior (solid line) or interstitial rope channel (dotted line). The inset shows the energetics of a typical diffusion path calculated for Li moving through an open nanotube.

→ Our group: Poizot et al. Nature, 407 (6803), 496-499 (2000).

Microstructure evolution of RuO₂ after Li-insertion and extractio

μ m-RuO₂ + 4 Li \rightarrow 2 Li₂O/Ru (2-5 nm) \rightarrow nm-RuO₂

P. Balaya, H. Li, J. Maier, Adv. Func. Mater., 13, 621(200

Microstructure evolution of TiF₃ caused by Li insertion/extraction

 $\lim_{t \to \infty} \operatorname{TiE} \sum_{t \to \infty} \operatorname{LiE} \operatorname{Ti} (\operatorname{amorphous})$

A scheme for back-reaction LiX + M \rightarrow MX ?

diffusion of either Mⁿ⁺ or Xⁿ⁻ across the interphase : MX

LiX and M dispersed at atomic or nanoscale is key point or occurrence of back-reaction in view of kinetics. Experimental data confirm this!

Fig. 9. Lattice parameters of hexagonal unit cell of Li_xCoO_2 [18,22,23] (filled symbols represent monoclinic phases parameters converted to hexagonal parameters).

Comparison of morphology of LiCoO₂ before (a) and after surface coating with MgO (b), SnO_2 (c) and Al_2O_3 (d).

>电荷转移和净电荷(电离度)

-方面,对给定的M,可以通过分析LiM_{0.5}Mn_{1.5}O₄ $\Pi M_{0.5}Mn_{1.5}O_4$ 来理解脱嵌的影响。 <u> 不难发现,由脱嵌引起的电荷转移主要</u> 来自O,而不是Mn和M. 另一方面,可以通过比较 $LiM_{0.5}Mn_{1.5}O_4$ 中M上的 争电荷,来分析不同掺杂的影响。我们可以看出, /In上的净电荷基本不受M的影响(这与以前的结论 一致

🖴 Mandaratan un mer de Manasa de antie Oliveire que la Presenta de Strader de Mandarat de 1988 de 1988 de la Antie Presidente de State de Mandarat de Mandar

Slow electronic conductivity: How to bypass this handicap?

$Li FePO_4$ 的能带和态密度图

纯的LiFePO₄是一种典型的半导体,其理论上的带隙为0.53eV.费 米能级附近的窄带是Fe的3d部分.Fe的非成键 t_{2g} 态和反成键 e_{g} 态分别位于-1~-0.11eV和0.28~1.5eV的能量范围。

对Li FeP04和Li 1-3/32Cr1/32FeP04的比较

实验证实3%铬掺杂可以提高磷酸铁锂电子电导8个数量级

Migration Energy Barriers of Li and Cr ions in the LiFePO₄ crystal along the one-dimensional diffusion pathway.

路漫漫而修远兮,....

谢谢!