US-China Electric Vehicles and Battery Technology Workshop, China 2011

北京理工大學
BEIJING INSTITUTE OF TECHNOLOGY

团结 勤奋 求实 创新

中国废旧电池的回收与再利用技术现状

Current situation of recycling and reusing for spent batteries in China

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内容提要 Outline

1. 我国目前的废旧电池回收现状
   The current status of spent battery recycling in China
2. 废旧电池综合回收利用技术
   Recycle and recovery technologies of spent batteries
3. 国内典型电池回收企业
   Typical battery recycling companies in China

Challenge and Opportunites of Power Battery

1.Performance and Safety

2.Cost Reduction

3.Battery Recycling

✓ **From the viewpoints of environmental preservation, recovery of major components or valuable resources, and provision of raw materials, the battery recycling is highly desirable in either the present time or the future.**

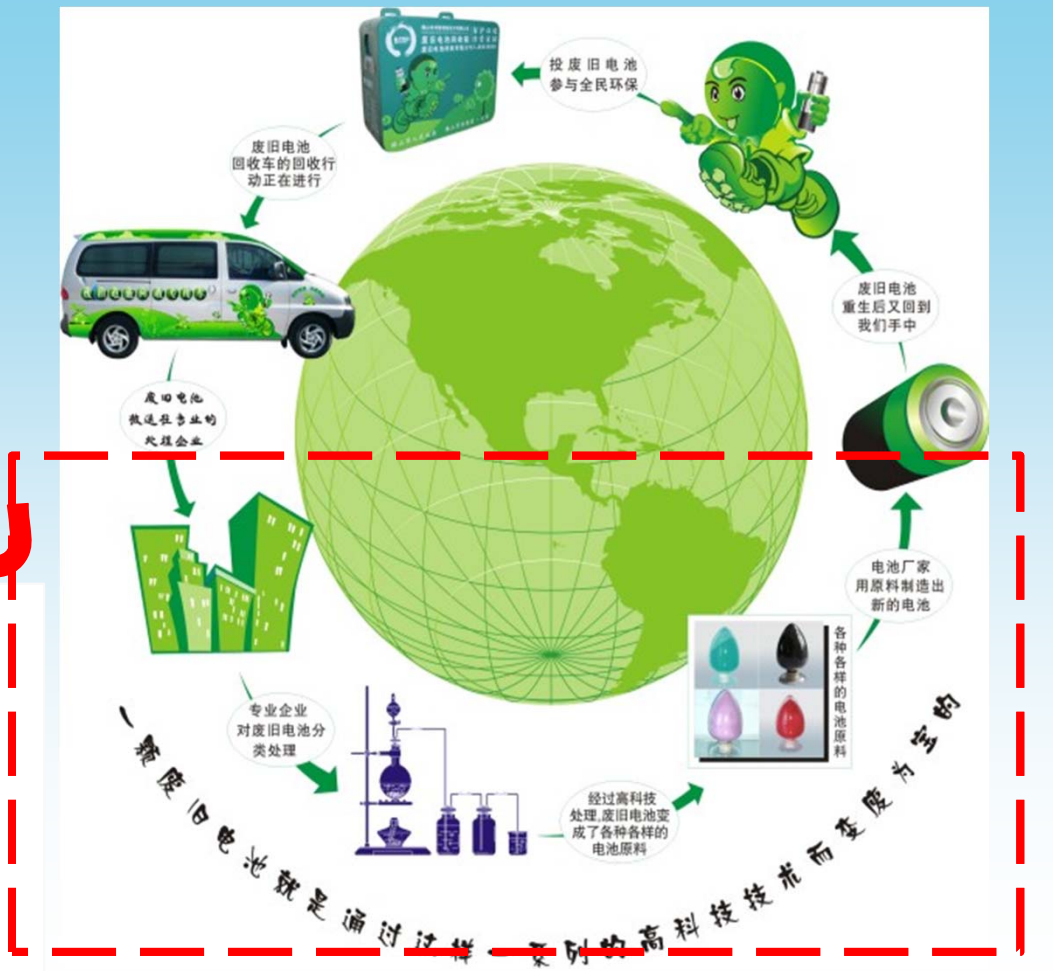
“中国废旧电池回收体系”是在政府的规范引导下、通过多种渠道、多种方式、集合多种社会多种资源体，所共同搭建起的一种可以将废旧电池有效环保回收、无害化处理、资源化再生，并能自我存续和持续固定的一种资源循环利用体系模式。

Under the guidance of the government's regulations and specifications, wasted battery recycling system in China is a self-survival and continued fixed resource recycling system model . It supplies an effective way to recycle, reduce and reuse for wasted batteries.

根据回收所针对的主体的不同，可分为“上游”和“下游”两类

According to different recycle subjects, it can be divided into "upstream" and "downstream”

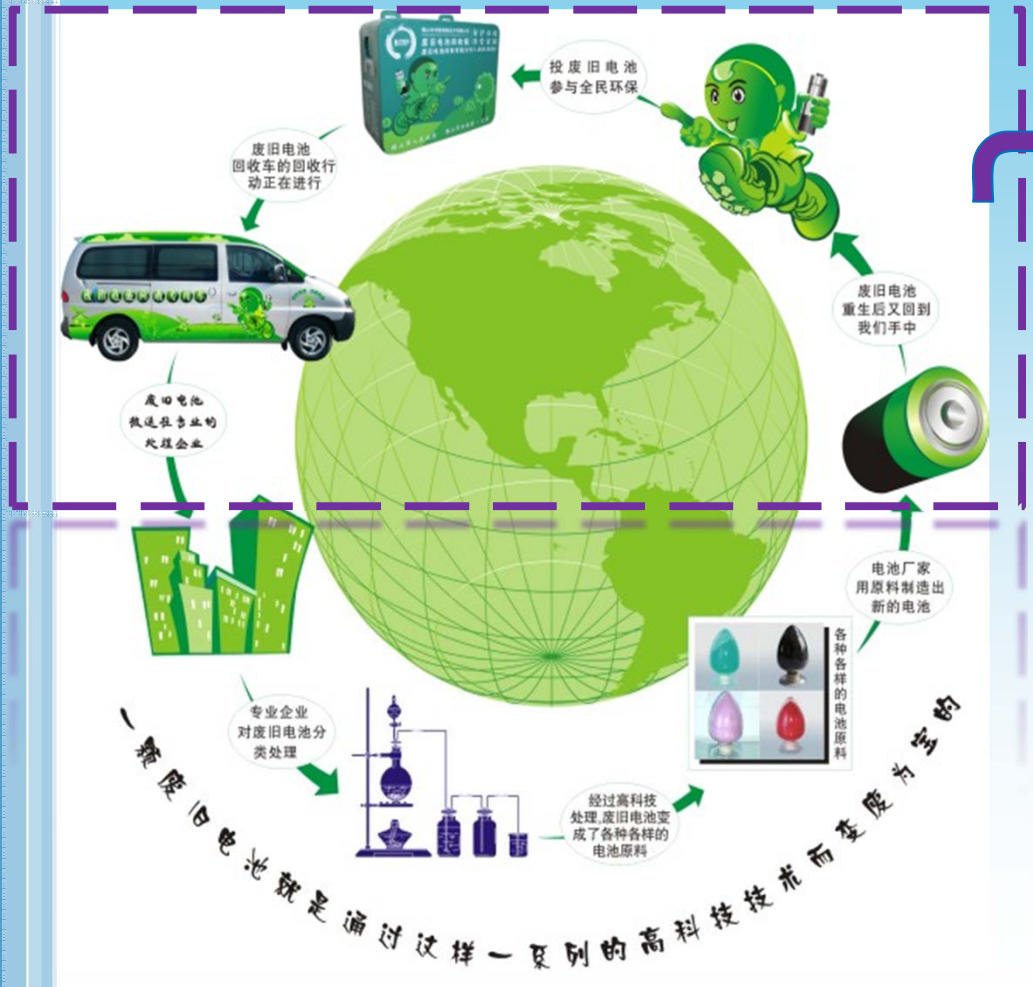
- 上游–电池生产企业生产过程中所产生的不良品、报废品、召回品等废旧电池的回收处理问题；上游回收以商业模式为基础。



- **Upstream – battery manufacturers**
  Defective products, scrap and recalled products arising from production process, and other issues of recycling; Business Model

根据回收所针对的主体，可分为“上游”和“下游”两类

According to different recycle subjects, it can be divided into "upstream" and "downstream”



● 下游–电池消费者

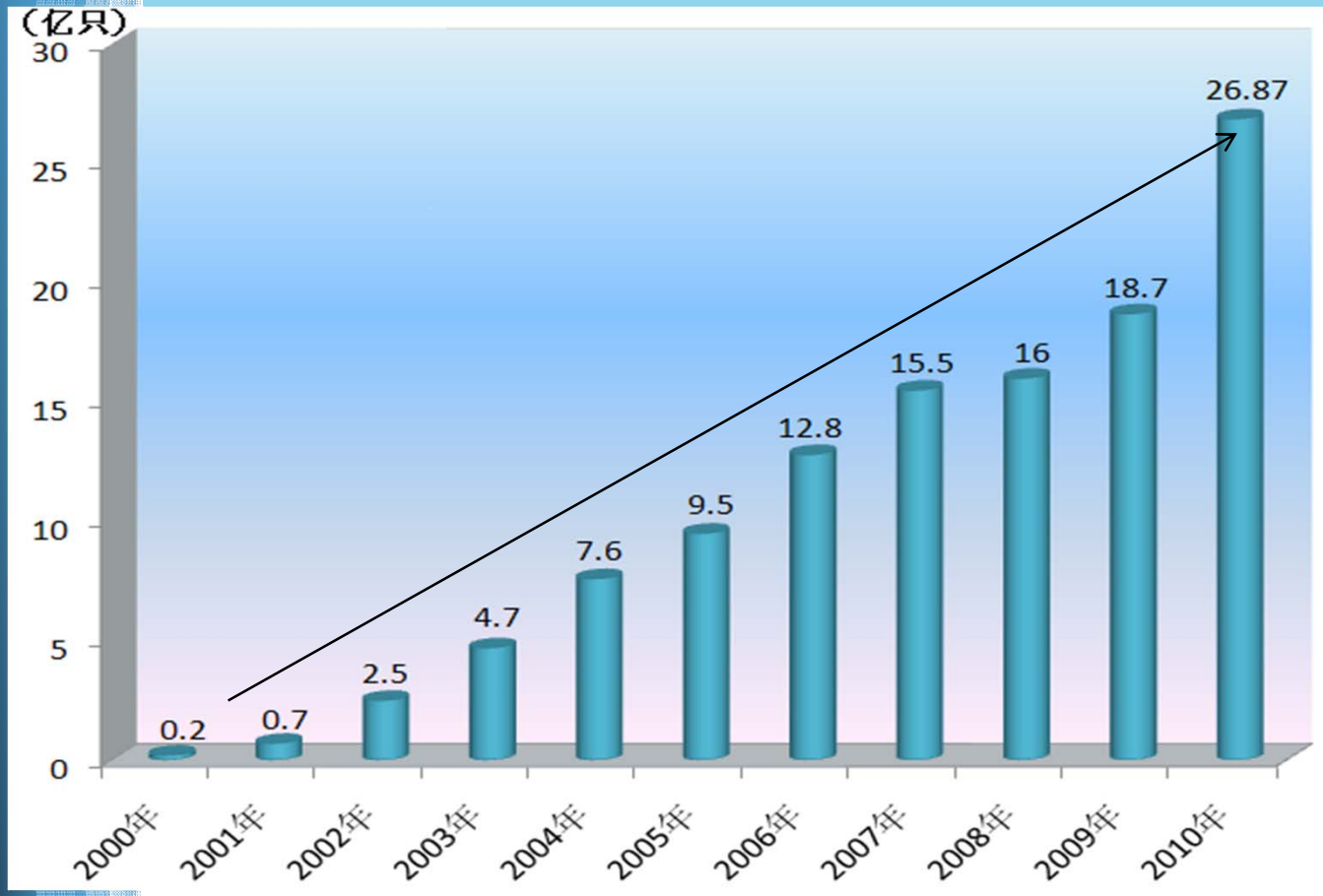
使用报废之后的废旧电池回收处理问题；下游回收以公益模式为基础，以社会公德、责任心为依归，是社会文明进步的表现。

●Downstream - Battery consumers

wasted battery recycling issues after degradation; Public Service

It depends on social ethics, social civilization and progress.

我国锂离子电池产量
Production of LIB in China



DATA FROM: CHINA BATTERY INDUSTRY ASSOCIATION

锂离子电池的使用量和废弃量

World production and consumption of LIBs

2000年5亿只
500million units

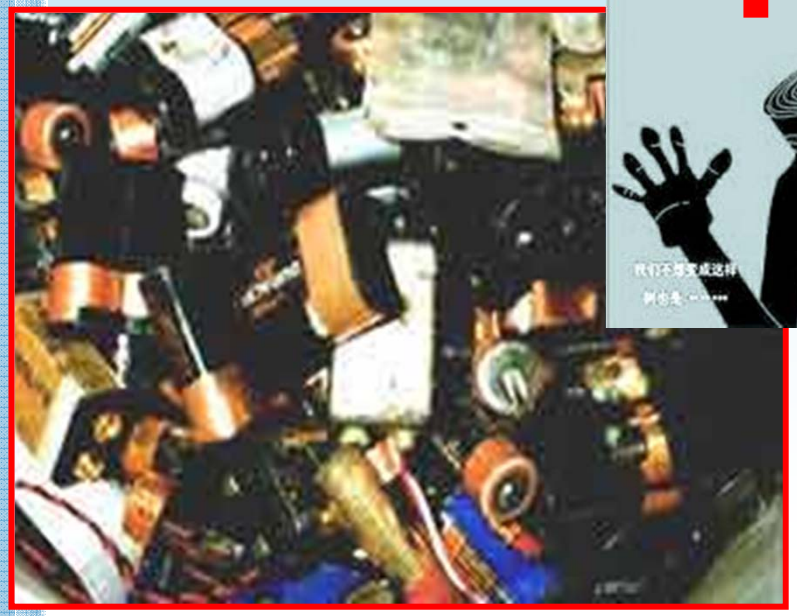
2004年9亿只
900million units

2010年46亿只
4.6billion units

使用年限2年
年平均废弃量200-500吨
Amount of waste:200-500t/y

Dry batteries

Button batteries



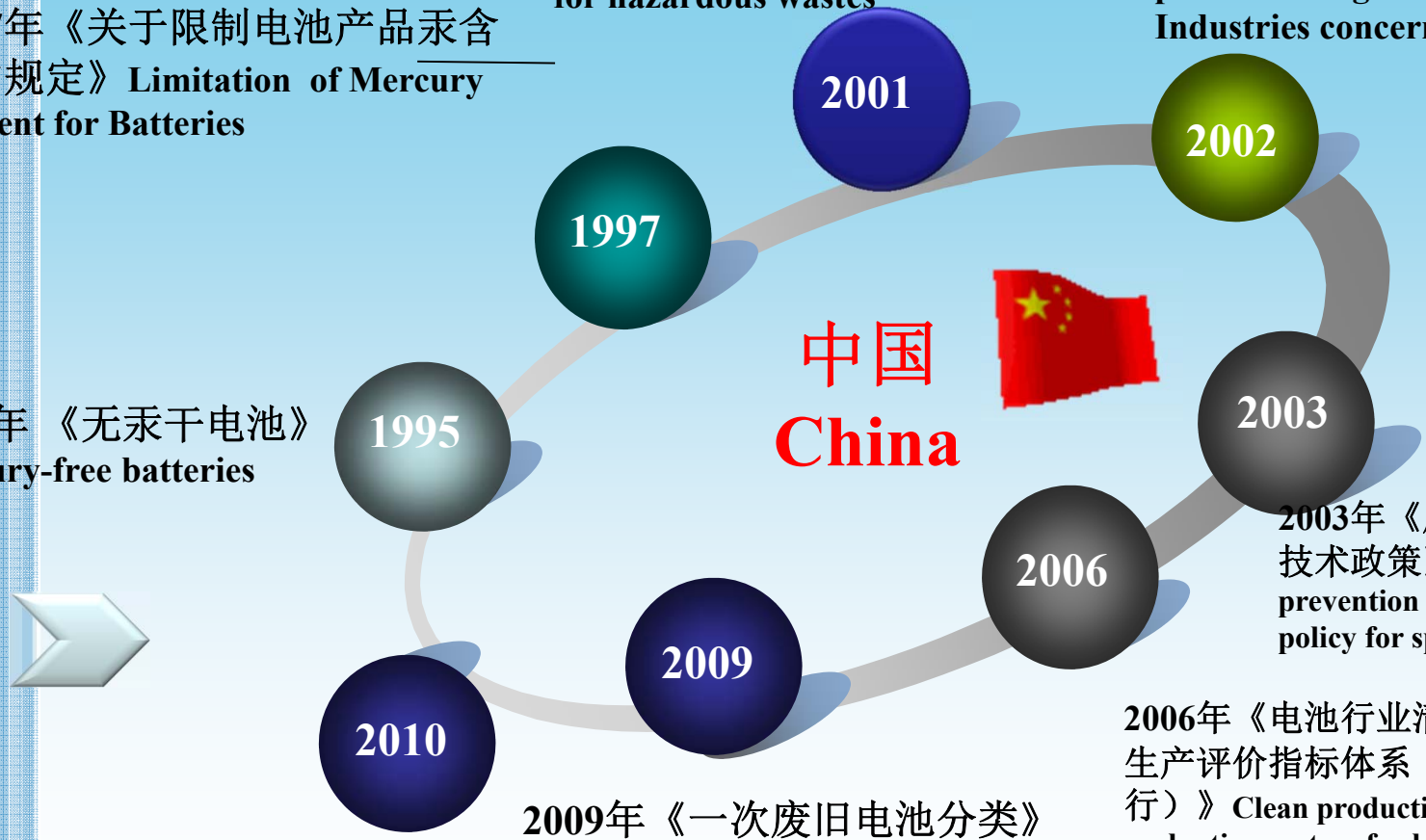
Ni/MH batteries

Li-ion batteries

2001年《危险废物污染防治技术政策》Technology policy of pollution control for hazardous wastes

2002年《关于涉汞行业环境保护管理规定》Environmental protection regulations for Industries concerning mercury

1997年《关于限制电池产品汞含量的规定》Limitation of Mercury Content for Batteries



1995年《无汞干电池》Mercury-free batteries

2003年《废电池污染防治技术政策》Pollution prevention and technology policy for spent battery

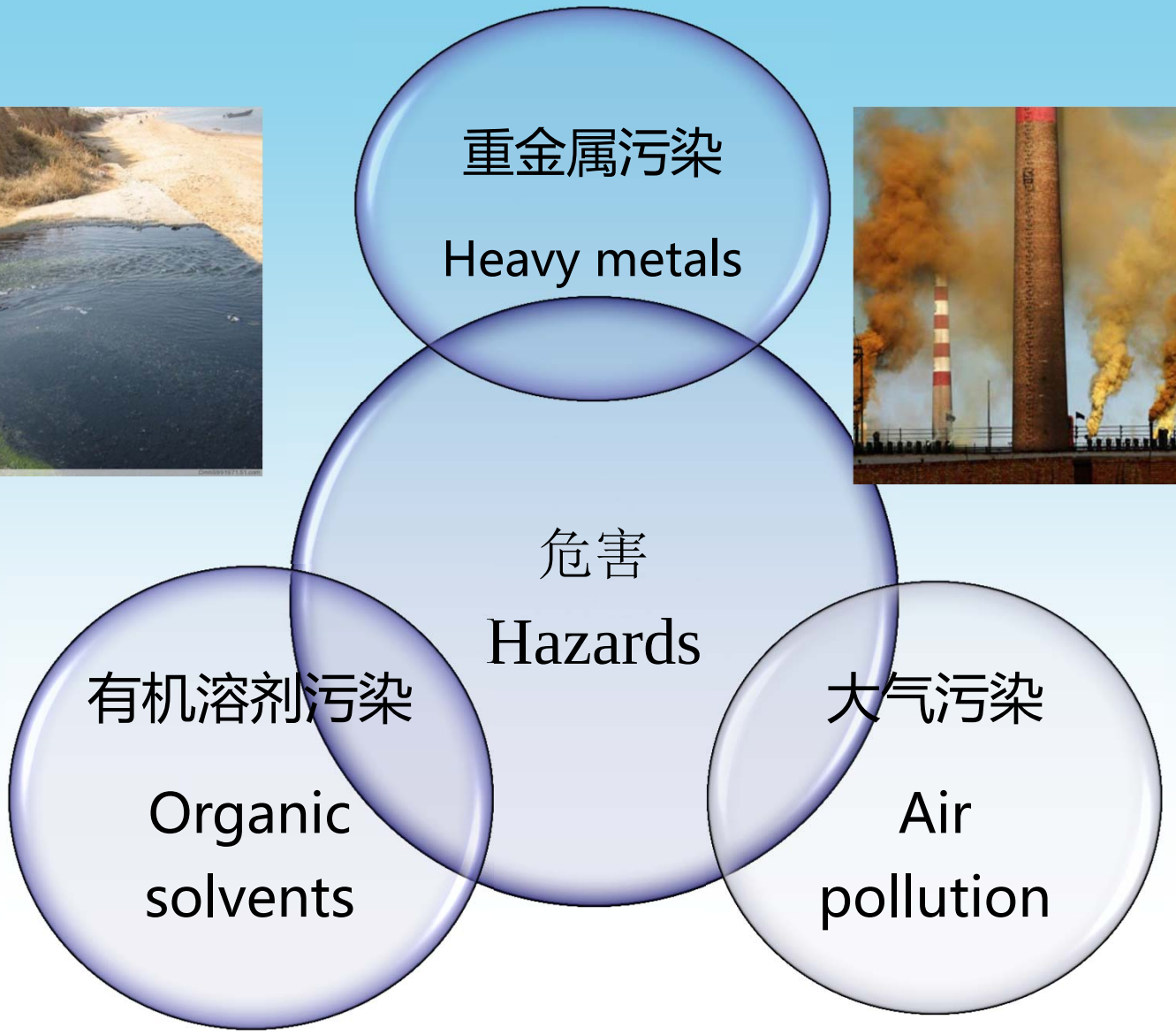
2006年《电池行业清洁生产评价指标体系（试行）》Clean production evaluation system for battery industry

2009年《一次废旧电池分类》和《二次小型电池废料废件分类》推荐性国家标准 Recommended National Standards of the classification of waste dry battery and second battery

2010年《废弃电器电子产品回收处理管理条例》Regulations for recycling of waste electrical and electronic products

废旧电池产生的危害

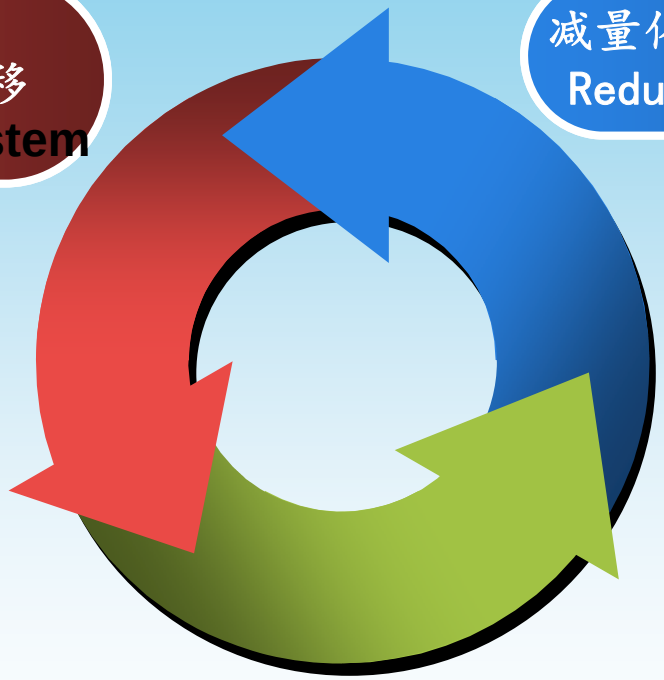
Safe disposal may become a serious problem due to the presence of flammable and toxic elements or compounds



废旧电池污染防治的原则
Principles of pollution control for spent battery

全过程控制
避免二次污染和污染转移
total process control system

减量化、资源化和无害化
Reduce, Reuse, Recycle



突出重点、分类控制
Target key points, classified control

回收与利用

废旧二次电池回收处理技术
Processes and technologies for the recycling of spent batteries

酸浸过程(Acid leaching)
生物淋滤(Bioleaching)
化学沉淀法(Chemical precipitation)
溶剂萃取法(Solvent extraction)
电化学法(Electrochemical process)

化学法
Chemical treatment

直接合成电极材料
Direct synthesis of electrode materials

溶胶凝胶法(Sol-gel method)
水热法(Hyrdothermal method)
共沉淀法(Co-precipitation method)
电化学法(Electrochemical method)

物理法
Physical treatment

火法(Thermal treatment)
机械分离(Mechnical separation process)
研磨过程(Mechanochemical process)
有机溶剂溶解(Dissolution process)

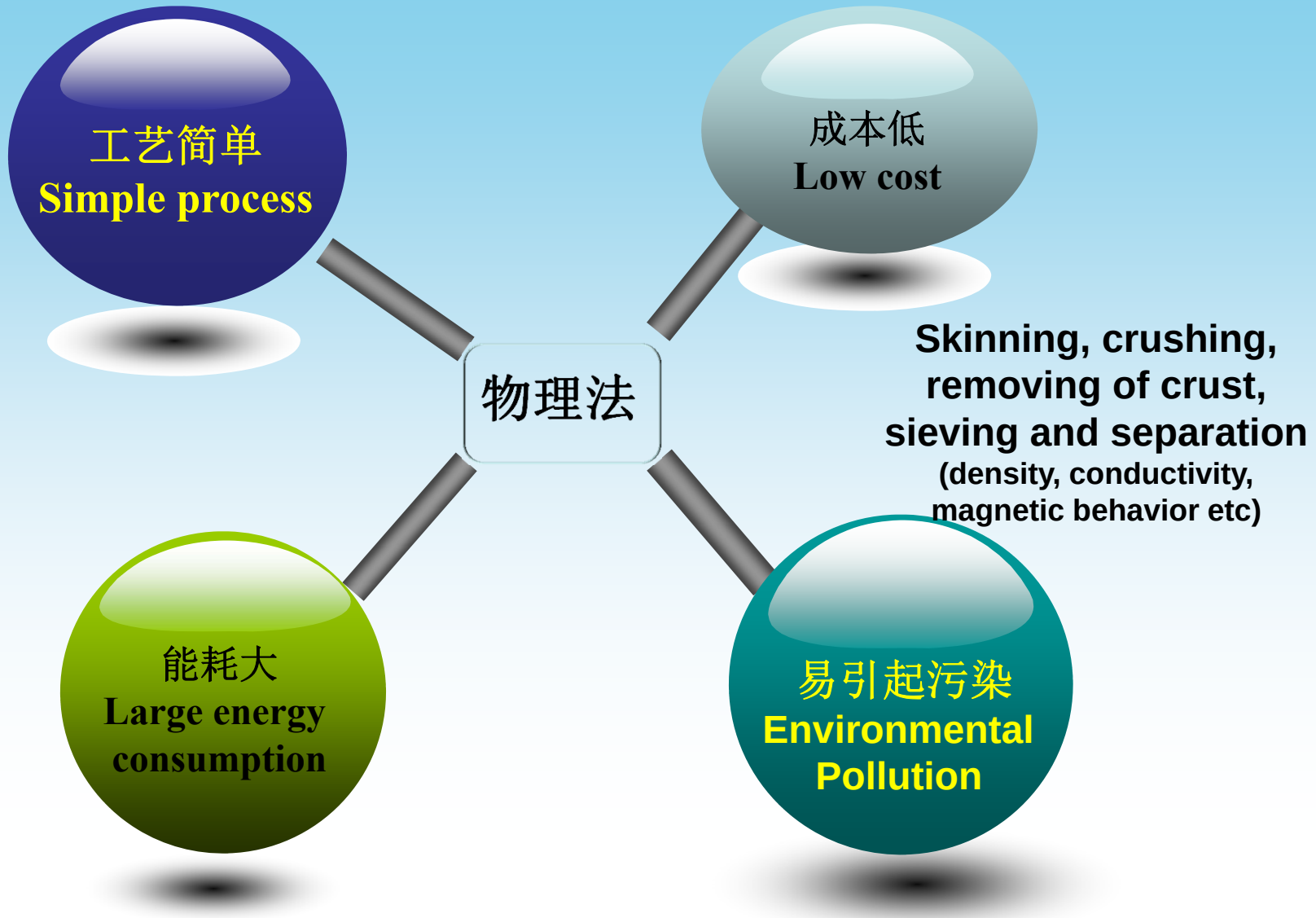
Summary of recycling processes or treatment methods for the components of lithium-ion batteries

Components	Elements	Recycling processes	References
Shells	Fe	Mechanical processes; thermal treatment	[9,4,11,14]
	Plastics	Mechanical processes	[9,11]
Aluminum foil	Al	Mechanical processes; acid leaching; chemical precipitation	[9,11]
Anode	Cu	Mechanical processes	[9]
	C (graphite)	Mechanical processes; thermal treatment	[9,4,35]
Adhesive agent	PVDF binder	Thermal treatment	[4,5]
Electrolyte (organic liquid—$LiPF_6$, $LiBF_6$, $LICIO_4$)		Thermal treatment; solvent extraction	[4,27,34]
Cathode ($LiCoO_2$, $LiNiO_2$, $LiMnO_4$)	Co	Mechanochemical process; dissolution process; thermal treatment; acid leaching; bioleaching; solvent extraction; chemical precipitation; electrochemical process	[1,4,5,11,14,23,26,31,34,35, 39,40,43,50–53,55]
	Li	Mechanochemical process; thermal treatment; dissolution process; acid leaching; bioleaching; Solvent extraction	[1,4,5,11,14,23,26,31,34,35, 39,40,43,50–53]
	Ni	Mechanochemical process; chemical precipitation; electrochemical process	[4,28,40]
	Mn	Chemical precipitation	[4]

A single recycling process can only achieve the destination of recovering a part of components or can only be one step of a whole procedure for recycling spent LIBs. Therefore, combination of several single recycling processes is necessary to recycle or recover the main components from spent LIBs.

Journal of Power Sources 177 (2008) 512–527

(1) 物理法(预处理) Physical method (Pretreatment)



机械研磨法 Mechanochemical process

钴酸锂材料与PVC共研磨

研磨后Co和Li与PVC中的氯生成无机氯盐

用水溶解，可与其他研磨物质分离

Co-grinding of $LiCoO_2$ with polyvinyl chloride(PVC)

↓

Formation of Li- and Co-chlorides

↓

Water leaching

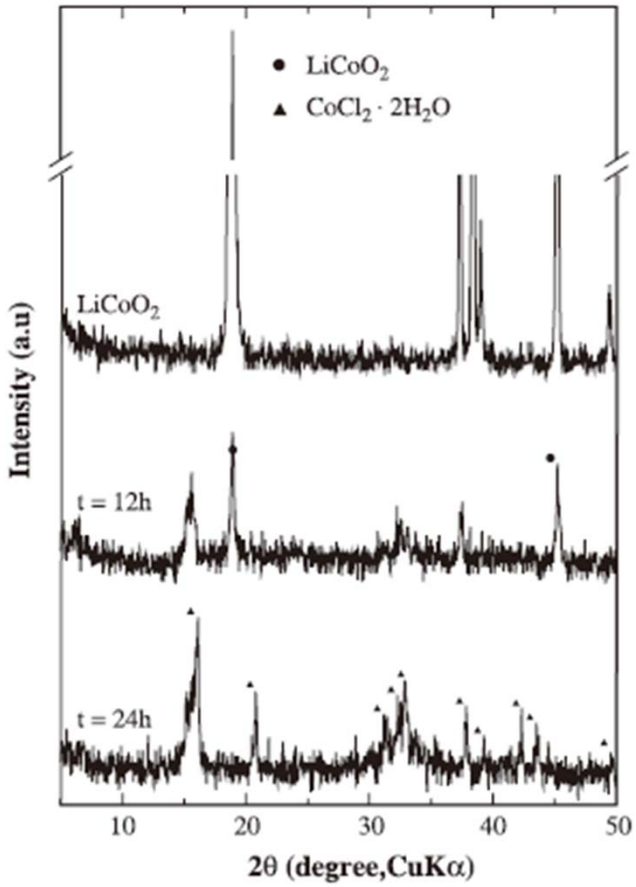


Fig. 1. XRD patterns of the mixtures of $LiCoO_2$ and PVC ground for different periods of time.

90%Co & almost 100%Li can be recovered. About 90% of chlorine in PVC sample transformed into inorganic chlorine.

(2) 化学法 *Chemical processes*

化学处理法
Chemical processes

酸浸或生物淋滤

Acid leaching

Bioleaching

沉淀法
(Chemical precipitation)

溶剂萃取法
(Solvent extraction)

电化学法
(Electrochemical process)

一、天然有机酸对钴酸锂电极材料的浸出研究

（1）柠檬酸对钴酸锂电极材料的浸出研究

Leaching process for $LiCoO_2$ materials using citric acids as leachant

Spent LIBs from cellular phones

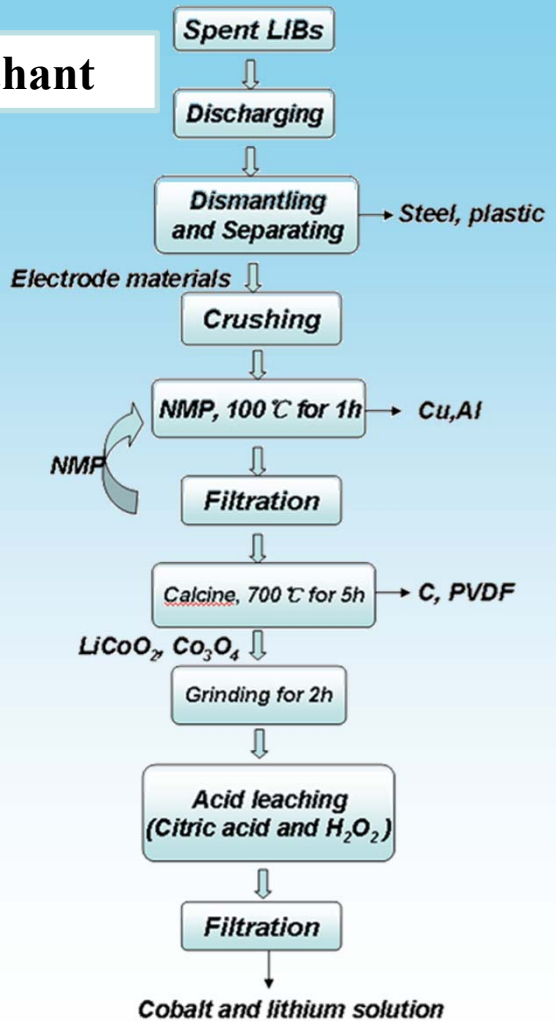


Table 1
Li, Co, Mn and Ni content in cathodic active material of the spent LIBs.

Element	Content (w/w)
Li	4.40%
Co	53.8%
Mn	0.97%
Ni	0.80%

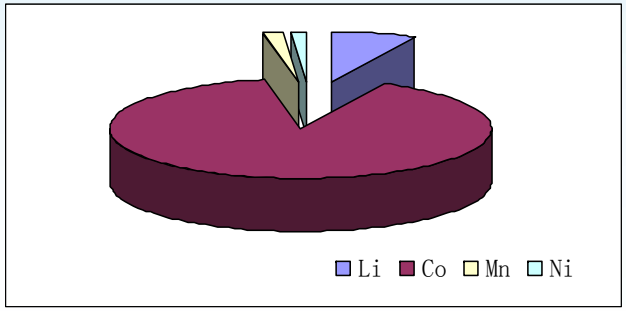
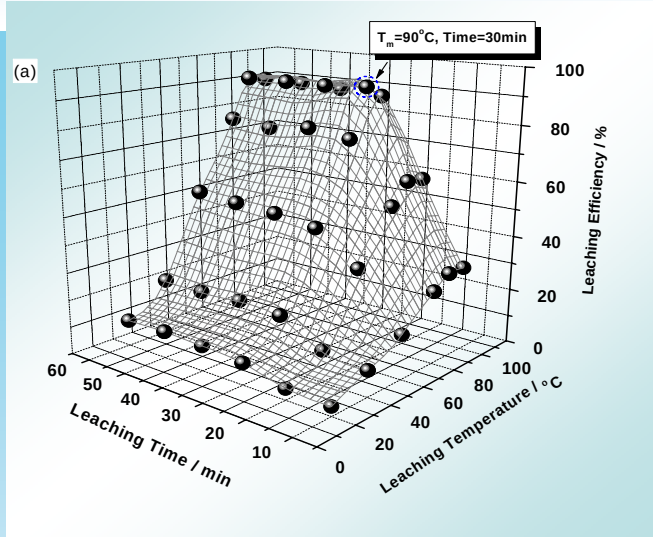


Fig. Flowsheet of the hydrometallurgical recycling process for lithium ion secondary rechargeable batteries.



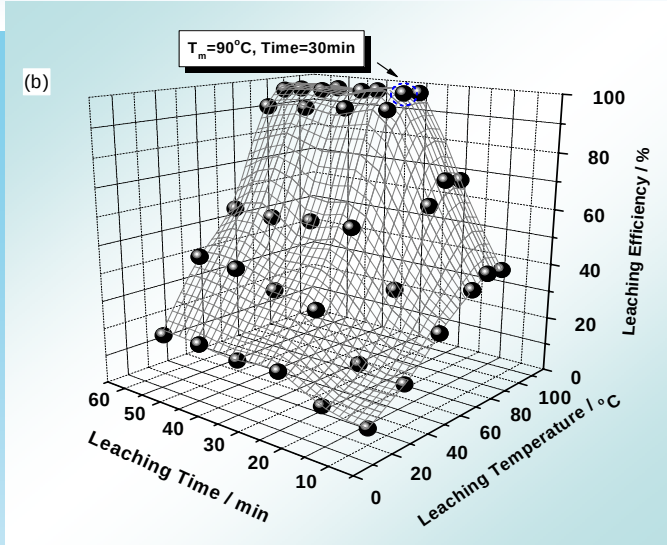


Fig. 6. Effect of leaching temperature and leaching time on the leaching of waste LiCoO2 with 1.25 M citric acid

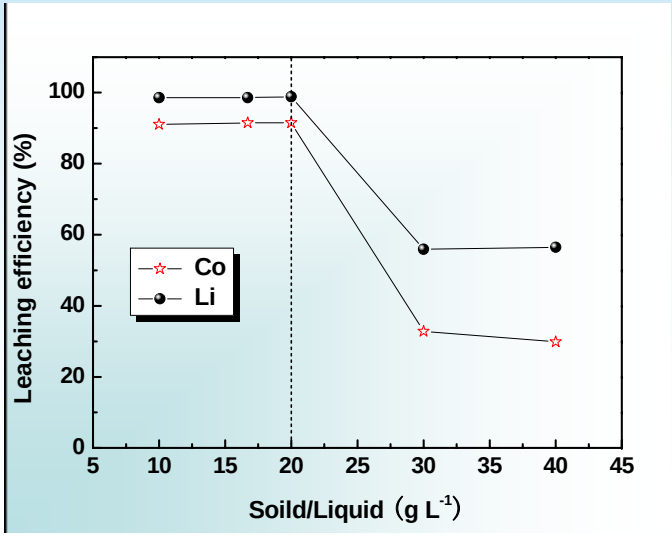


Fig. 7. Effect of solid/liquid ratio on the leaching of waste LiCoO2 with 1.25 M citric acid at 90 °C for 30 min

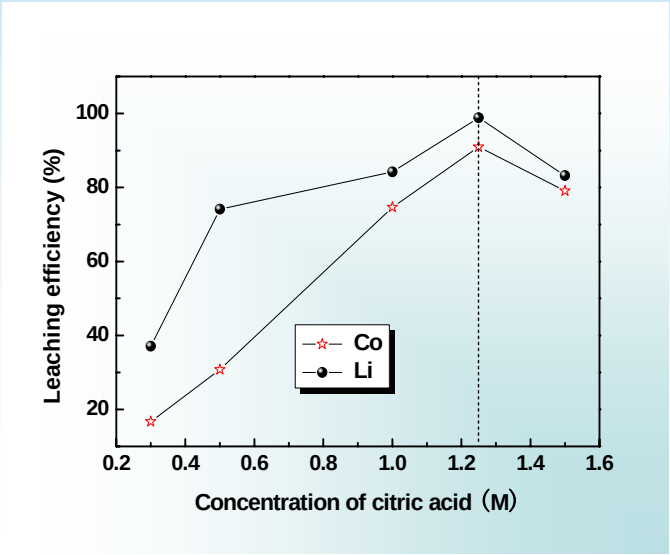


Fig. 8. Effect of citric acid concentration on the leaching of waste LiCoO2 at 90 °C for 30 min

L.Li, J. Ge, F. Wu et al， J. Hazard. Mater.176 (2010), pp. 288-293

（2）苹果酸对钴酸锂电极材料的浸出研究

Organic acid leaching using malic acids

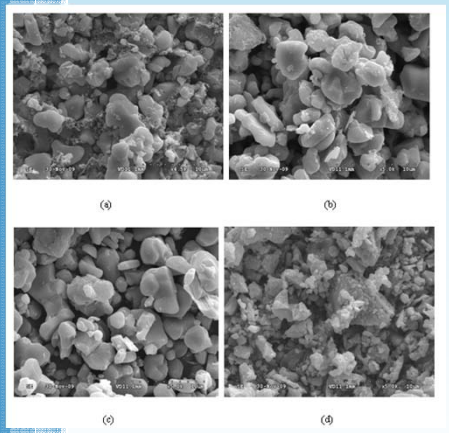


Fig. 1. SEM images of different cathode materials: (a) the dismantled cathodic material from a spent LIB, (b) the cathodic material after treatment with NMP, (c) the cathodic material after dismantling and calcination at 700 °C for 5 h and (d) the leach residues.

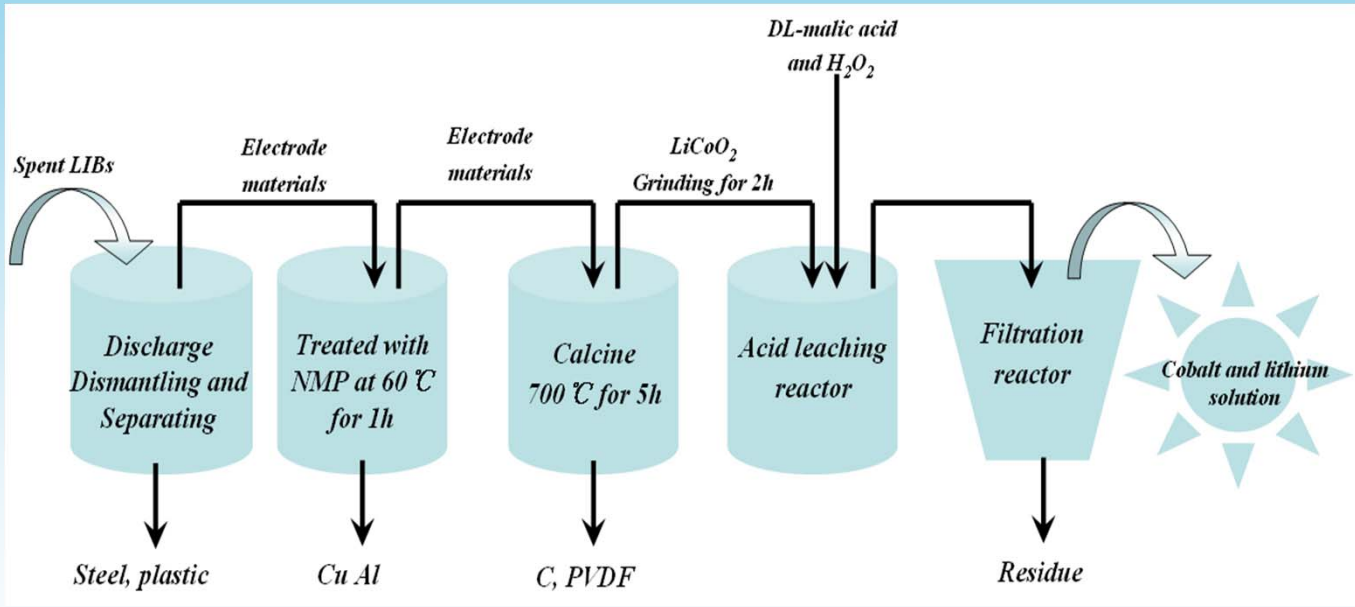


Fig. 2. Flow sheet for the recovery of Co and Li from spent Li-ion batteries using DL-malic acid as a leachant

（2）苹果酸对钴酸锂电极材料的浸出研究

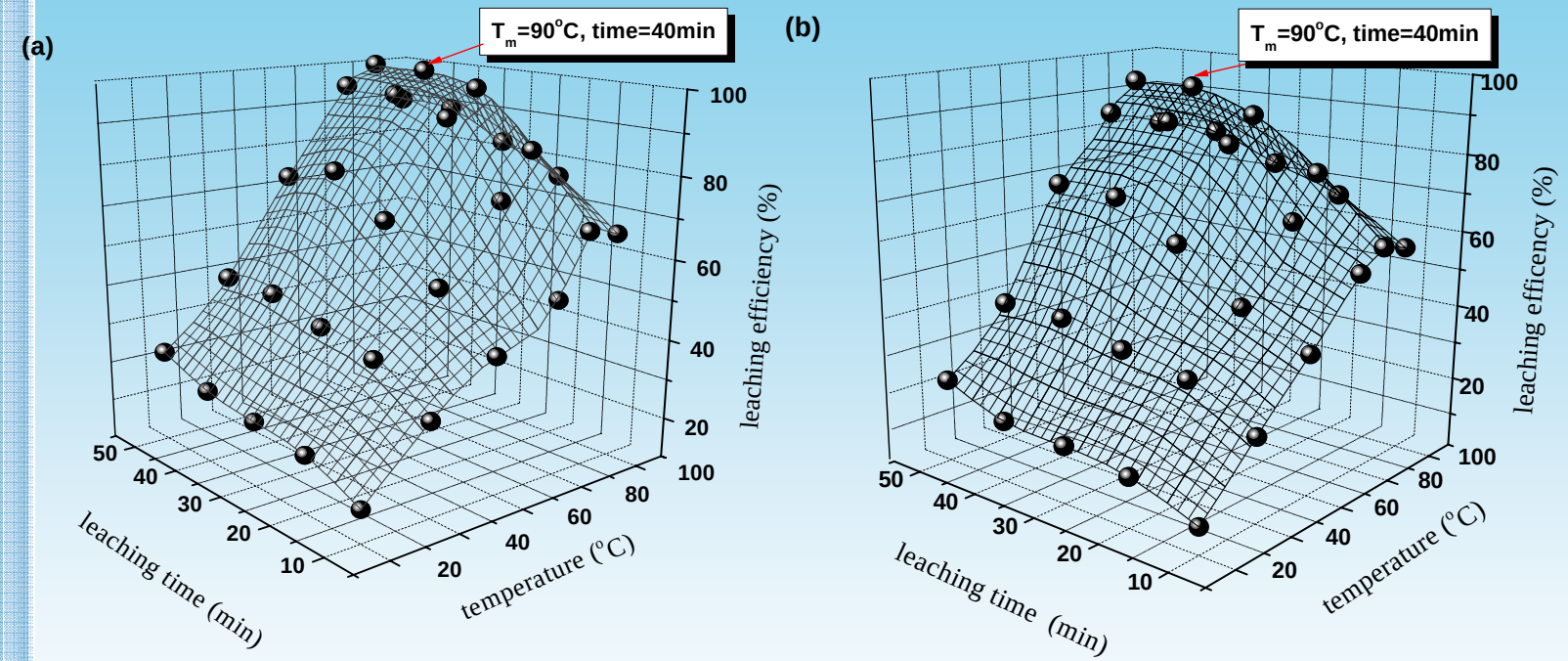


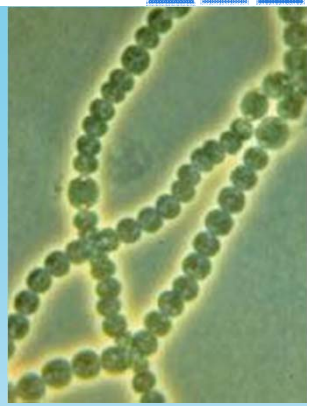
Fig. 6. Effect of leaching temperature and leaching time on the leaching of waste LiCoO2 with 1. 5 M malic acid (H2O2=2.0 vol.%., S:L= 20 gL−1 and agitation speed=300 rpm) leaching efficiency of Li and (b) leaching efficiency of Co.

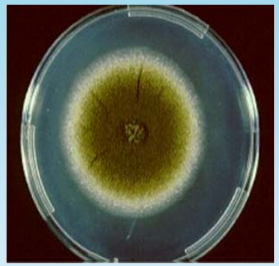
(Using 1.5 M DL-malic acid, 2.0 vol.% hydrogen peroxide, a leaching temperature of 90 ℃, a S:L ratio of 20 g/L and a time interval of 40 min nearly 100 wt.% Li and more than 90 wt.% Co were extracted.

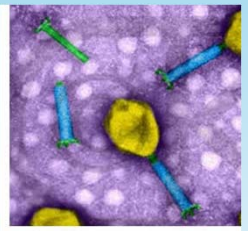
Li Li, Jing Ge, Feng Wu et al， Waste Management, 2010，30： 2615-2621

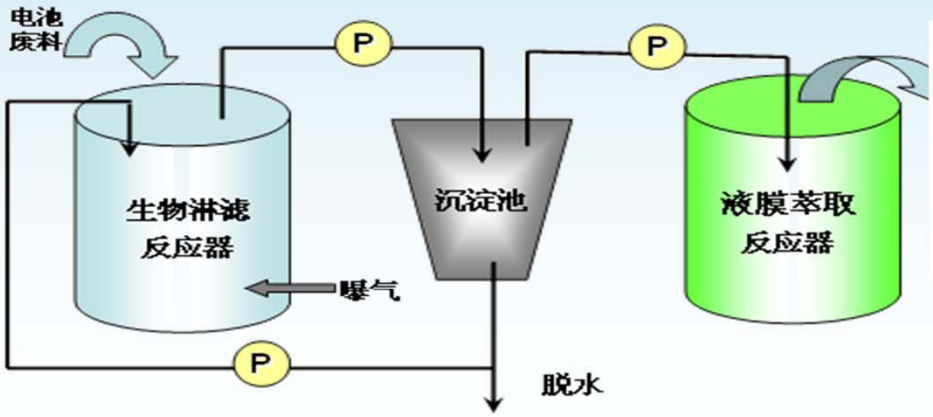
三、生物淋滤技术　Bioleaching process

- Bio-hydrometallurgical processes have been gradually replacing the hydrometallurgical one due to their higher efficiency, lower costs and few industrial requirements.
- Using special bacteria which utilized elemental sulfur and ferrous ion as energy source to produce metabolites like sulfuric acids and ferric ion in the leaching medium.

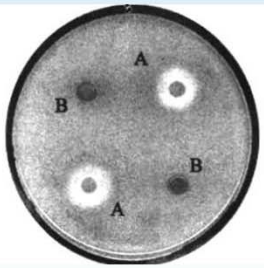


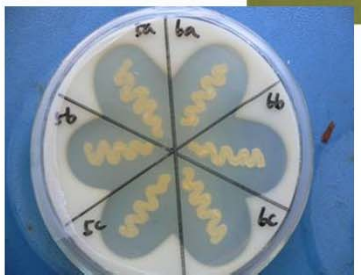






生物淋滤--液膜萃取法工艺流程

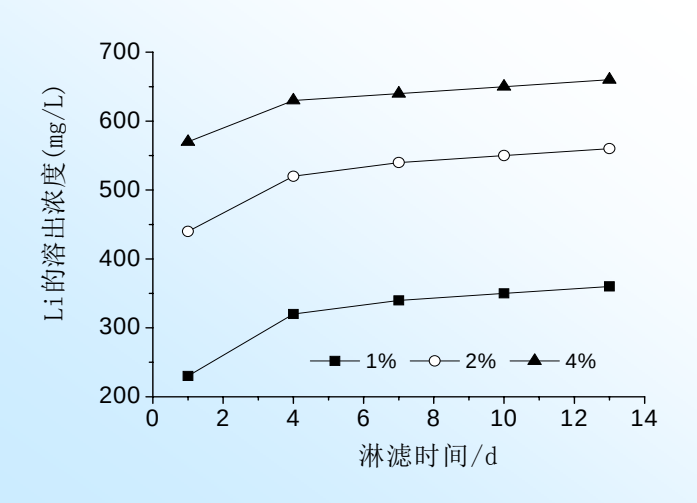


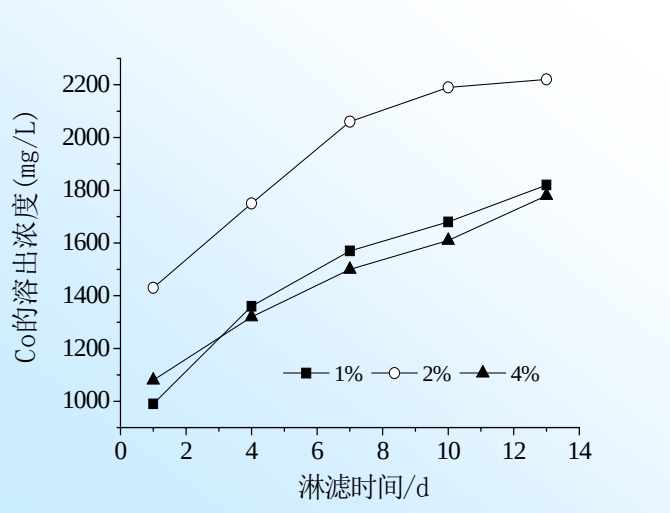


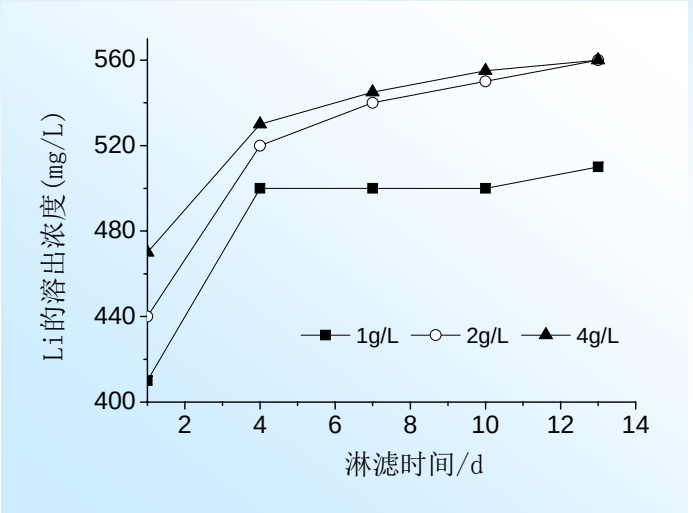
Morphology

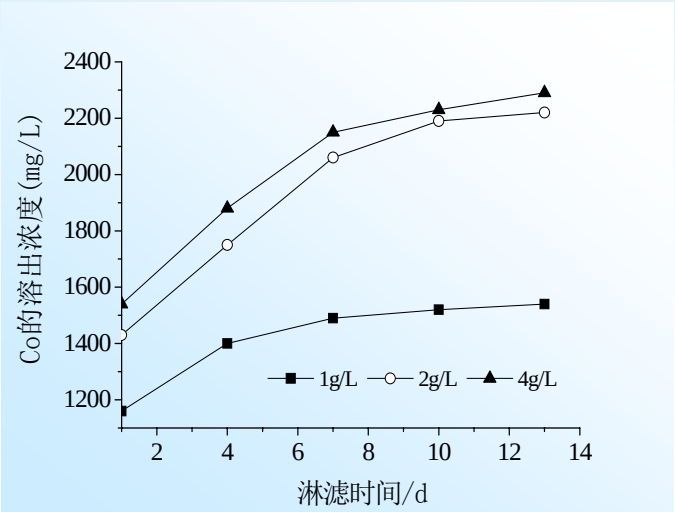
固液比和硫源浓度对金属离子的生物溶释效率影响

Effect of S/L and Sulfur concentration on leaching efficiency of metals in Bio-leaching









Bioresource Technology，100：6163–6169，2009.

国内典型电池回收企业–1

Typical battery recycling companies in China-1

深圳市格林美高新技术股份有限公司
Shenzhen Green Eco-manufacture Hi-tech Co., Ltd

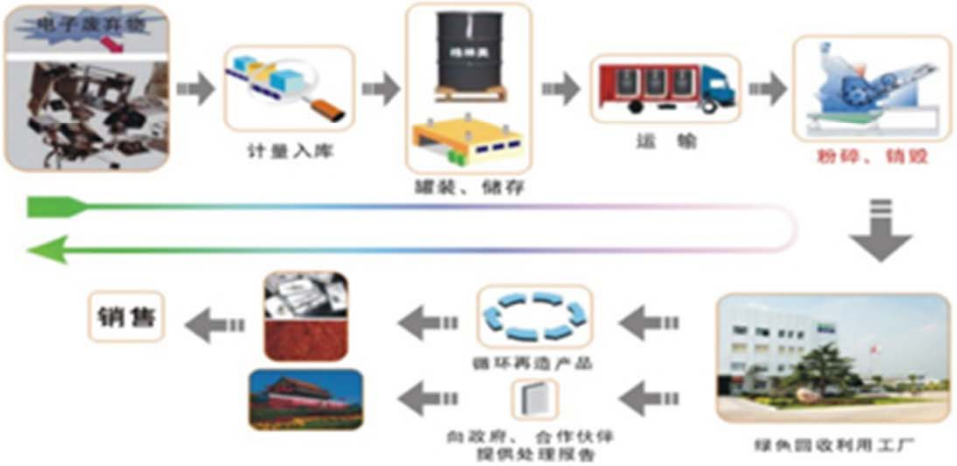
废旧电池回收再生工艺流程图

The flowchart of recycling process for spent batteries

可循环利用的电子废弃物：

消费者用过的电话、洗衣机、冰箱、电视机、空调、微波炉、风扇、电饭煲、电脑、录像机、复印机、传真机等各种生活电子产品；生产过程中产生的电路板、集成电路、报废电子产品等各种电子配件与产品。

全程监控电子废弃物的收集、运输、销毁和再造过程，保障不让一件电子废弃物流入黑市或非法通道。100%按约定销毁，100%循环再造。

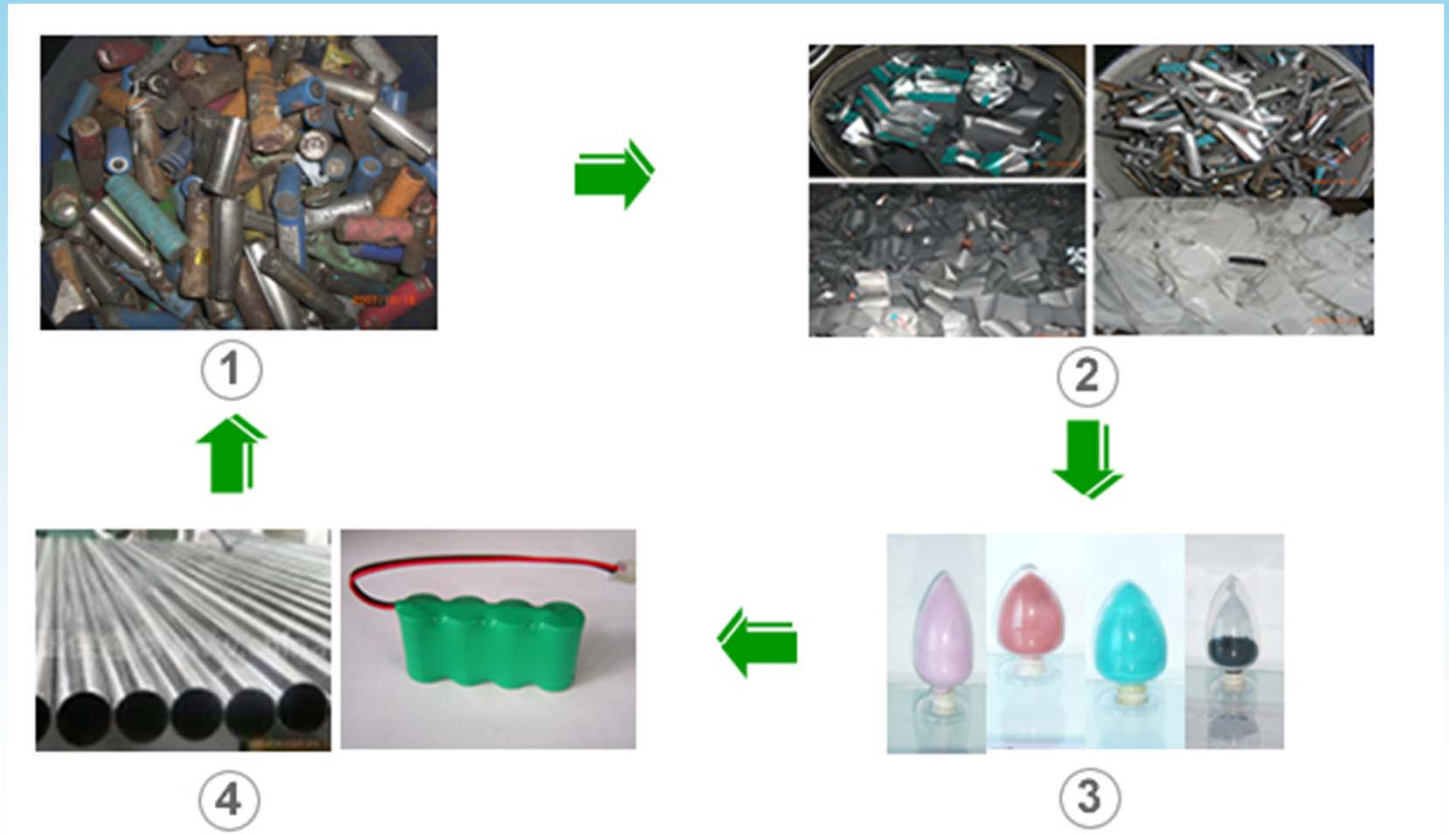


国内典型电池回收企业-2

Typical battery recycling companies in China-2

佛山邦普镍钴技术有限公司

FUOSHAN BANGPU NI/CO HIGH-TECH CO.,LTD



废旧电池资源桥接式循环演示中心

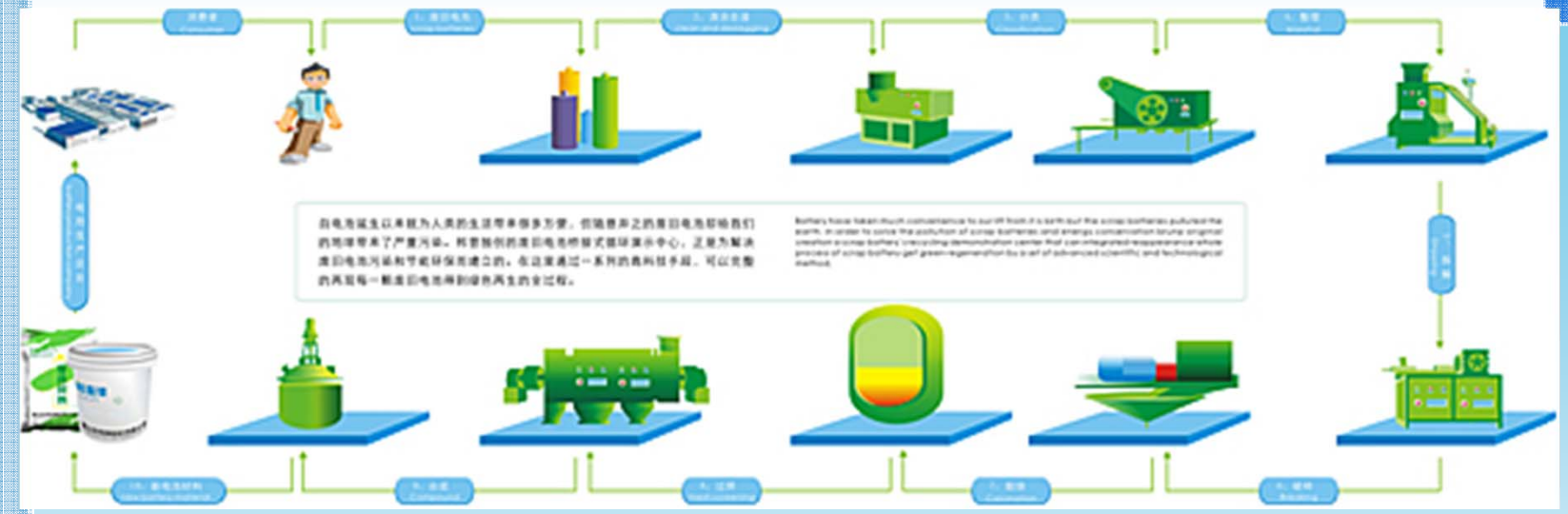
Demonstration center of recycling process for spent batteries

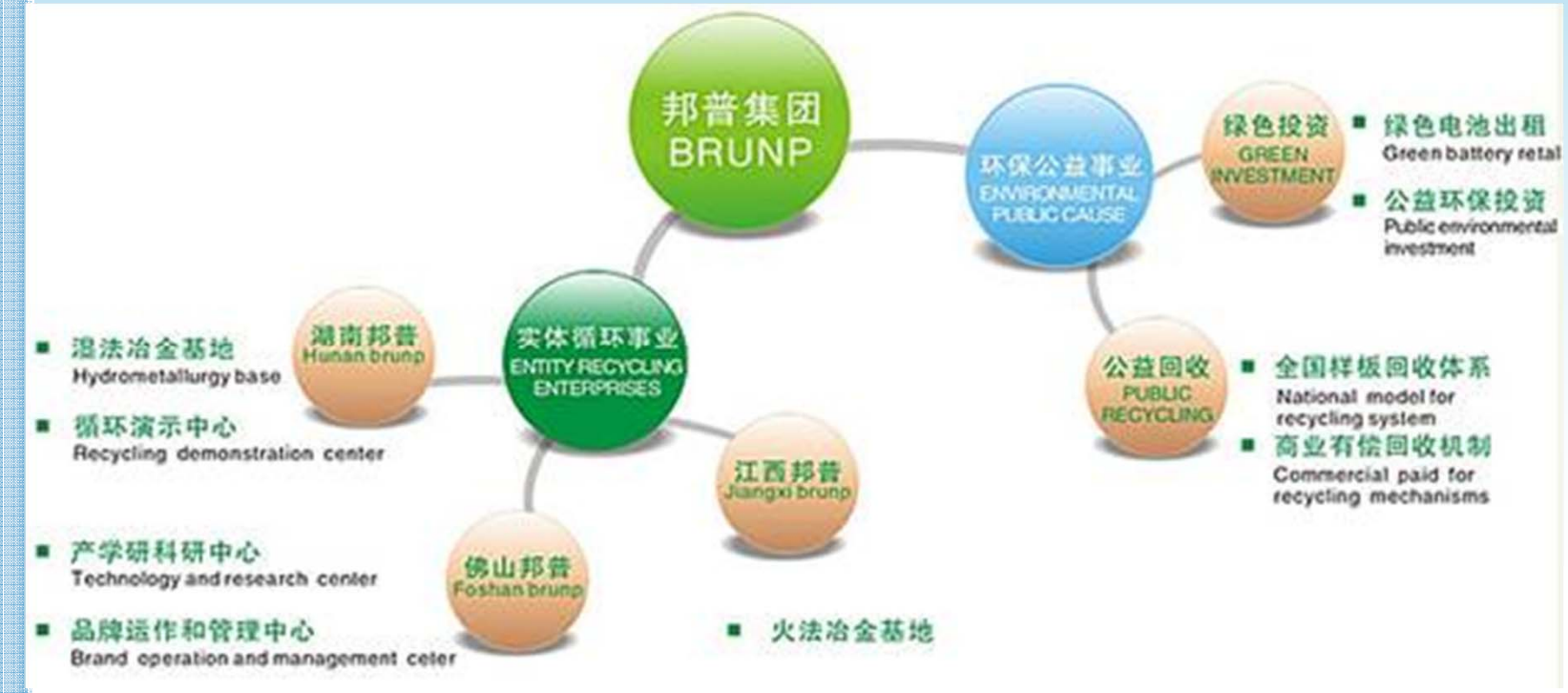
湖南邦普循环科技有限公司

2010/01/16 13:32

A
B
REFRIGERATION

硝酸镍

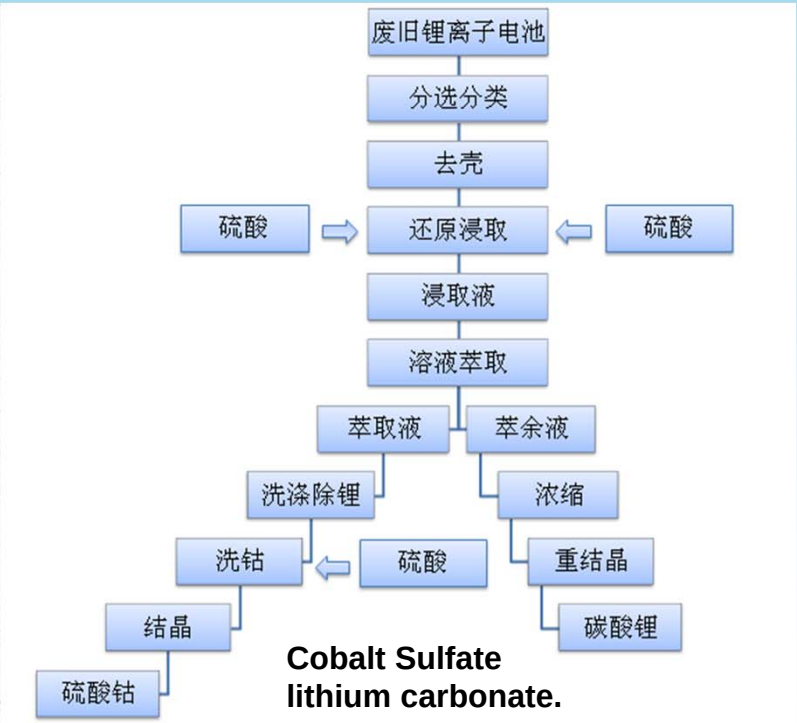



邦普集团
BRUNP
环保公益事业
ENVIRONMENTAL PUBLIC CAUSE
绿色投资
GREEN INVESTMENT
绿色电池出租
Green battery retal
公益环保投资
Public environmental investment
实体循环事业
ENTITY RECYCLING ENTERPRISES
湖南邦普
Hunan brunp
湿法冶金基地
Hydrometallurgy base
循环演示中心
Recycling demonstration center
产学研科研中心
Technology and research center
品牌运作和管理中心
Brand operation and management ceter
佛山邦普
Foshan brunp
江西邦普
Jiangxi brunp
火法冶金基地
公益回收
PUBLIC RECYCLING
全国样板回收体系
National model for recycling system
商业有偿回收机制
Commercial paid for recycling mechanisms

国内典型电池回收企业-3

Typical battery recycling companies in China-3

泰力废旧电池回收技术有限公司
SHENZHEN TAILI WASTE BATTERY RECYCLE. CO.,LTD



It is still necessary to develop an efficient collection system in order to receive the spent LIBs consumed around the world and recycle the spent LIBs.

Thanks for your attention!

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