Lab of Renewable Energy and Energy Safety
Institute of Chemical Defense

Safety and Toxity Analysis for Materials of EV Power Li-ion Battery

4th US-Cina Electric Vehicle and Battery Technology Workshop

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1 Necessary of This Work

1 Necessary of This Work

1.1 Why

到2015年，中国以电动车、混合动力车、氢燃料电池车为主的新能源车将达到100万辆，因此，有关安全和环境的重大问题就摆在行业面前。

1 million EV will go on road by 2015, We are going to face big problems of Safety and Enveronment.

★ 动力锂电池由于多次事故的发生，其安全性越来越受到重视.

EV Li-ion batterys‘ safety get more and more attention for the many accidents happening.

★ **电池的安全性**指在各种测试条件下不出现泄露、冒烟、着火、爆炸等现象，在滥用条件下人员与设备不受伤害。

Battery safety issues concern fairly local damage. Abuse of batteries typically results in leaks ,package rupturing or burst that can result in personal injury , equipment damage

★ 锂动力电池用材料中的电解液、隔膜、添加剂是有机物，一旦发生安全事故，可能泄露有毒物质对人员和环境造成危害。

Once the Li-ion battery EV safety accident happened, the leaked toxics resulted in personal injuryand environmental problems.

1 Necessary of This Work

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1.2 What

按现有交通事故频率、损失状况、电池内容物泄露、电池更换废弃与回收现状来看，城市环境可能会面临某些问题和压力。

According to now transportation accident frequency, damage, toxic leakages, battery change and recycle situation, cities environment will have to face some problems .

表 1 全国-北京历年交通事故情况统计(2000—2011)

年份	汽车保有量（万辆）	汽车事故率%	万车死亡率	汽车保有量（万辆）(北京)	万车死亡率(北京)	致死率%(北京)	直接经济损失(万元)
2000	1608.90	1.026	15.60	150.7	9.8	11.88	
2001	1823.50	1.000	15.40	169.6	8.7	13.88	6267.0
2002	2382.90	0.873	15.24	176.5	7.8	14.34	4112.0
2003	2421.20	0.692	10.82	212.4	7.73	16.61	4361.4
2004	2693.70	0.484	10.01	229.6	7.1	19.69	4057.9
2005	3159.70	0.369	8.09	258.3	5.87	21.99	2915.5
2006	4416.70	0.263	6.20	287.6	4.77	20.55	2771.9
2007	5099.60	0.205	5.10	320.2	3.78	18.89	2620.2
2008	5696.80	0.158	4.37	350.1	2.81	21.77	2066.6
2009	6280.60	0.128	3.64	400.1	2.44	15	1987.3
2010	9086.00	0.096	2.63	480.9	2.03	7	2000.0
2011	9363.60	0.100	2.97	490.00		1.5(2015)	

It is necessary to do works:

★ 对各种竞争动力电池的安全性评估

Safety evaluation to competetive EV batteries

★ 对电池材料毒物谱系分析、危险品及级别界定

Aanalysis to materials' toxicy, define the hazard class of EV Li-ion battery

★ 电池爆炸及有毒内容物泄露后的应急与防护

Defense , response and rescure steps for the sfety accident , battery burst and leakage.

2 Hazard Classification of Li-ion Battery

2 Hazard Classification of Li-ion Battery

2.1 U.S.

美国交通部已将锂离子电池归类为危险品，是一种包括易燃性、浸出毒性、腐蚀性、反应性等有毒有害性的电池，是各类电池中包含毒害性物质最多的电池，不能随便运输，需要特殊的包装箱、包装方法，各种标签要齐全才能输运，而且空运更有多种限制，要通过锂电池UN38.3认证．

Li-ion Battery had been classified as hazard goods, it is a kind of toxic and harmful battery including flammability, toxity, causticity and active reaction, containing the most toxic matters, which can not been transported optionally. It need authentication by UN38.3.

但这并没有动摇美国政府推动锂动力电池产业的决心，在联邦政府能源部支持下，美国阿贡实验室牵头，14家美国电池与先进材料公司组建了国家交通用先进电池制造联盟，以促进美国车用锂离子电池的制造能力。

However, Li-ion Battery's toxity and hazard charecteristicsn never changed the mind of the US government to impel the EV and EV Li-ion battery industry development. Under the support of the Union DOE, with the leading of Argonne, 14 US companies of battery & advanced materials had set up National transportation advanced battery manufacture Union to promote EV Li-ion battery manufacture ability.

2 Hazard Classification of Li-ion Battery

2.1 U.S.

联盟将谋求在美国建立一个或多个供联盟成员共享的制造与原型开发中心。为形成大规模制造锂离子动力电池的能力，预计未来5年将需要投入10-20亿美元。大部分投资将来自于联邦政府。针对政府的资金帮助，电池联盟将统一使用，而非各自为获得小部分支持资金而竞争。

The Union tried for building one or more manufacture development centure to share ,and to form a cosmically EV Li-ion battery manufacture ability.

美国安全测试和认证公司保险商实验室（Underwriters Laboratories，简称UL）计划推出一系列有关电动汽车电池的新规范。随着人们对电动汽车的兴趣不断增长，美国保险商实验室通过一份声明表示，“新的规范将帮助人们规避火灾等危险，提高电动汽车电池的整体安全性”。

UL planed to make a series of new standards and criterions for EV batteries and large batteries, to help people avoid fire danger, to increase the whole safety of EV battery manufacturing.

2 Hazard Classification of Li-ion Battery

2.2 China

在国家科技部支持下以清华大学、北京理工大学研发团队为首的国内动力锂电池先进制造联盟正积极促进国内动力锂电池产业的发展和相关规范和标准的制定工作。

Under the support of MOST, Tsinghua, BIT and other battery and advanced materials enterprises are promote Chinese EV Li-ion battery manufacture development and relative series of new standars and criteritions constitution actively.

电池是电动汽车的关键部件。但由于目前报废的锂电池并不属于国家规定的危险废弃物，这无形中造成了废旧锂电池在回收管理上的空白。目前国家并没有明文规定废旧锂电池的处理方法。电池的使用成本和维护成本相当高。

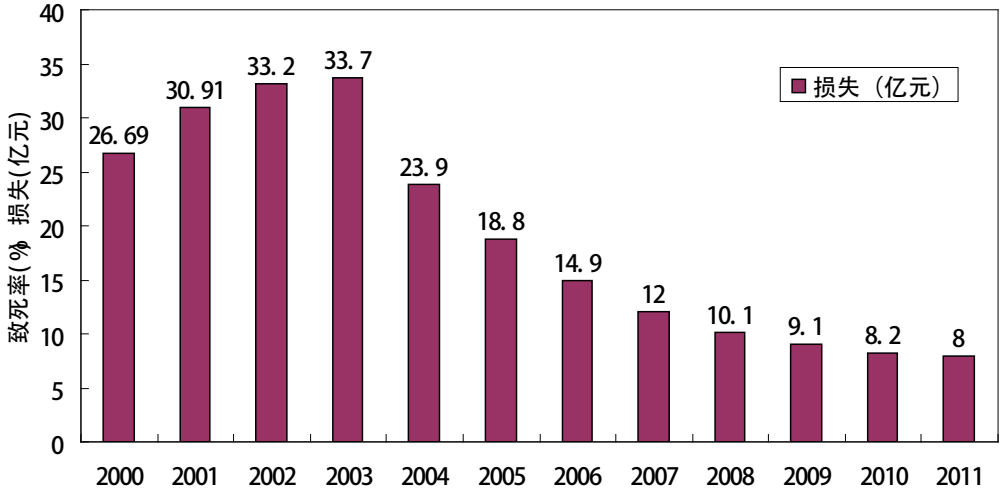
Battery is the key parts of EV.
But now in China, the abandoned Li-ion battery are not included in hazard abandon matters, which results in a blank zoon in the management recycling of abandon batteries. Neither formal legale rules for the abandoned and old battery's treatment in China.
The cost of battery's usage and maintenance is quite high.

2 Hazard Classification of Li-ion Battery

2.2 China

中国历年交通事故死亡人数的官方统计稳居世界第一。2000年以来全国-北京交通事故情况统计和经济损失数据分析，每年因交通事故所造成的经济损失达数百亿元。

The sum number of death in transportation accidents in China is always the first over the world. The transportation accidents caused more than 10 billions direct economic damage every year.



2000- 2011年全国交通事故损失

按目前交通事故率类比，如果100万辆电动汽车上路，发生的交通事故，除死亡率、经济损失等其它数据，由于动力锂电池材料的复杂多样和毒性，可能增加动力锂电池内容物泄露，有毒气体释放、污染环境等问题。

According to the transportation accidents sum, there would be very high possibility arosing the battery toxic containes leakage, persona injury, environment pollution problems if there will be more than 1 millions EV run on the road by 2015.

3 EV Li-ion Battery Safety

3.1 Understanding

In general, battery safety issues concern fairly local damage. Improper use of batteries typically results in leaks ,package rupturing or burst that can result in personal injury , most certainly damage equipment and environmental problems.

- ★ Li-ion cells, have an electrode that is either liquefied or gelled that is flammable in both water and air, as well as is quite toxic.
- ★ Improper use can also lead to batteries getting too hot, which can also cause injury and damage equipment.

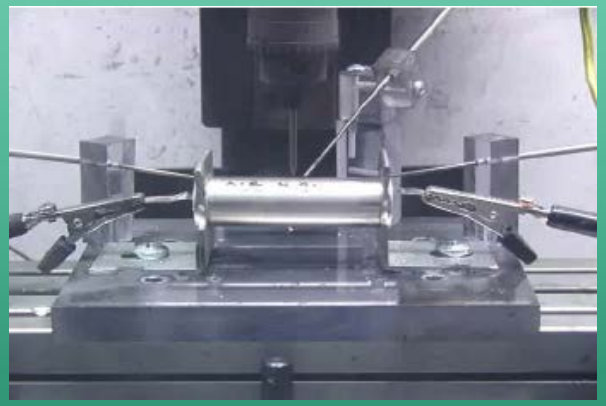
3.2 Reasons

Thermal reactivity of the battery components

- Overcharging of lithium batteries leads to irreversible damage to cell components and may cause serious safety problems.
- Discharging of the batttery release heat due to entropy changes, overpotentials, and ohmic resistance.
- SEI layer decomposition
- Positive active material decomposition with solvent oxidation
- Reactions between electrolyte, fluorinated binder and lithium metal

Internal short-circuit

Abuse behavior



4 Materials Spectrum of EV Li-ion Battery

4 Materials Spectrum of EV Li-ion Battery

动力锂电池在发生爆炸或燃烧等安全问题时，会产生一定量的有毒有害物质，具体种类与电极材料、电解质、溶剂、添加剂等材料有关。

When the safety accident happened about EV Li-ion battery, a certainty toxic and harmful matters would leaked out. The detailed kinds of toxic matters were relative with the electrods materials, electrolytes, solvents, additives and binders.

★ $LiPF_6$具有良好的导电性和电化学稳定性，是目前主流的电解质。但其存在两个缺陷：一是热稳定性不佳；二是对水分和氢氟酸（HF）敏感，容易发生分解反应。

$LiPF_6$ is the popular electrolytes for Li-ion Battery for its good conductivoty and chemical stability. But has two faults: (1) Thermal stability is not so good; (2)It is sensitive to moisture and HF,easy to decomposition.

★ $LiPF_6$在不同溶剂中形成的电解液的热分解，发现产物包括CO_2、C_2H_4、R_2O、RF、OPF_3、氟代磷酸酯、氟代磷酸和氧化乙烯齐聚物。

$LiPF_6$ will have different decomposition products in different solvents, include: CO_2、C_2H_4、R_2O、RF、OPF_3、fluorin substituted ester phosphate, fluorin substituted phoshate, and oxides of PE.

4 Materials Spectrum of EV Li-ion Battery

Reaction roads to toxic compounds:

$LiPF_6 \rightarrow LiF + PF_5$

$PF_5 + H_2O \rightarrow PF_3O + 2HF$

$2C_2H_5OCOOCH_3 \rightarrow C_2H_5OCOOC_2H_5 + CH_3OCOOCH_3$

$CH_3OCOOCH_3 + PF_5 \rightarrow CH_3OCOOPF_4 + CH_3F$

$CH_3OCOOPH_4 \rightarrow PF_3O + CO_2 + CH_4 + HF$

$CH_3OCOOPH_4 + HF \rightarrow PF_4OH + CO_2 + CH_3F$

$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOO\ PF_4 + HF + CH_2 = CH_2$

$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOO\ PF_4 + C_2H_5F$

$C_2H_5OCOO\ PH_4 \rightarrow PF_3O + CO_2 + C_2H_4 + HF$

$C_2H_5OCOO\ PH_4 \rightarrow PF_3O + CO_2 + C_2H_5F$

$C_2H_5OCOO\ PH_4 + HF \rightarrow PF_4OH + CO_2 + C_2H_5F$

4 Materials Spectrum of EV Li-ion Battery

SEI膜由稳定层(Li_2CO_3)和亚稳定层[$(CH_2OCO_2Li)_2$]组成，亚稳定层在90～120℃可能发生分解反应，放出热量，当温度高于120℃时，SEI膜不能保护负极，溶剂可能与金属锂或嵌入的锂发生反应，放出热量，产生气体，由此给电池、特别是动力电池造成很大的安全隐患。

SEI Film (Li_2CO_3, $(CH_2OCO_2Li)_2$)can not protect the cathode any more when the temperature is above 120℃. And will decompose to much more gases to cause safety danger.

★

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + \tfrac{1}{2}O_2$$

$$2Li + (CH_2OCO_2Li)_2 \rightarrow 2Li_2CO_3 + C_2H_4$$

$$2Li + C_3H_4O_3\ (EC) \rightarrow Li_2CO_3 + C_2H_4$$

$$2Li + C_4H_6O_3\ (PC) \rightarrow Li_2CO_3 + C_3H_6$$

$$2Li + C_3H_6O_3\ (DMC) \rightarrow Li_2CO_3 + C_2H_6$$

★

The binders, the solvents, the new Li, too.

5 Toxity Anslysis and Environmental Effection

表 2 电极材料的化学特性与潜在污染性

材料种类	材料名称	化学特性及危害
正极材料	$LiCoO_2$	与水、酸或氧化剂发生强烈反应。燃烧或受热分解产生有毒的锂、钴氧化物
	$LiFePO_4$ $LiMn_2O_4$	与有机溶剂或还原剂等反应产生有毒气体，受热分解产生氧气。
	$LiNiO_2$	受热分解为Li_2O、NiO和O_2，遇水、酸发生分解
负极材料	碳材料、石墨	粉尘与空气混合物遇火源爆炸，可与强氧化剂反应，燃烧产生CO及CO_2，嵌锂后与水作用生成强碱、自燃，可与氧气，氮气和酸等物质反应。
电解质	$LiPF_6$	有强腐蚀性，受热分解产生PF_5，遇水分解产生HF，燃烧产生P_2O_5等有毒物质。
	$LiBF_4$	强腐蚀性，与水、酸反应产生HF气体，燃烧或受热分解Li_2O、B_2O_3等有害物质。
	$LiClO_4$	强氧化剂，燃烧产生LiCl，O_2和Cl_2。
	$LiAsF_6$	溶于水，吸湿性强，与酸反应产生有毒气体 HF、砷化物等
	$LiCF_3SO_3$	燃烧产物为CO、CO_2、SO_2、HF，与氧化剂、酸反应生成HF。
电解质溶剂	EC、PC、DMC、EMC、DME 等	燃烧产生CO、CO_2，受热分解产生醛、酮等有害气体，部分会水解产生甲醇等有机物污染。
隔膜	PP、PE 等	燃烧可产生 CO、醛、有机酸等。
粘合剂	PVDF 等	受热产生 HF

5 Toxity Anslysis and Environmental Effection

5.1 Environmental

动力锂离子电池的电极材料在车体遭遇事故引发碰撞或爆炸燃烧，或废弃等状态下进入环境中，可与环境中其它物质发生水解、分解、氧化等化学反应，产生重金属离子、强碱和负极碳粉尘，造成重金属污染、碱污染和粉尘污染。电解质发生水解、分解、燃烧等化学反应，产生HF、含砷化合物和含磷化合物，造成氟污染和砷污染。溶剂经过水解、燃烧分解等化学反应，生成甲醛、甲醇、乙醛、乙醇、甲酸等小分子有机物，溶于水后造成水源污染。另外，电池在使用过程中因副反应而产生一些有害物质，如溶剂分解产物有丙烯、乙二醇、乙烯、乙醇等，电解质与正极电极作用的副产物有HF、LiF、CH_2OCO_2Li, CH_3OCO_2Li、CH_4、CO、CH_3OH等，负极同电解质发生副反应的产物，电极在预处理过程中加入的添加剂等，所有这些物质可直接或间接地造成环境污染。

When the EV battery happened a safety accident or abandoned to the environment, they could produce the below toxic matters:

HF, As compounds, P compounds, which would raise F, As pollution; HCHO, CH_3CHO, EtOH, HCOOH, could arose water source pollution; Propylene,qlycol, LiF、CH_2OCO_2Li, CH_3OCO_2Li、CH_4、CO、CH_3OH, are all toxics.

5.2 Human body

（1）氢氟酸
HF，由吸入、食入、经皮吸收引起健康危害。对皮肤有强烈的腐蚀作用，能穿透皮肤向深层渗透，形成坏死和溃疡，且不易治愈。 Blazing cauterization, which can penetrate skin, to form putrescence, not easy to cure.

（2）五氟化磷
PF_5，当六氟磷酸锂暴露于空气中或加热时，由于水蒸气的作用而迅速分解，放出五氟化磷而产生白色烟雾，对眼睛、皮肤，特别是对肺部有侵蚀作用。
Corrade effection to eye, skin and lung.

（3）甲基氟
CH_3F，吸入引起健康危害：高浓度有麻醉作用。眼或皮肤接触其液体(或正在快速蒸发的气体)会引起刺激和冻伤，但气体不会腐蚀皮肤。
Narcotism, frostbite.

（4）氟化锂
LiF，具刺激作用，吸入、食入、经皮肤吸收后会中毒。 Toxity.

（5）一氧化碳

CO，一种无色、无嗅的有毒气体，它与人体血红蛋白的结合能力是O_2的300倍，能阻止血红蛋白向人体组织输送吸收到的O_2。Toxic gas, can stop O_2 transportation to body.

（6）乙烯

C_2H_4，吸入引起健康危害：窒息性气体，具有较强的麻醉作用。Asphyxia gas, strong narcotism.

（7）乙烷

C_2H_6，健康危害： 高浓度时，有单纯性窒息作用。空气中浓度大于 6%时，出现眩晕、轻度恶心、麻醉症状； Asphyxia gas, giddy, nausea, narcotism.

（8）丙烯

CH_2=$CHCH_3$，对环境有危害，对水体、土壤和大气可造成污染。属低毒类，是单纯窒息剂及轻度麻醉剂。丙烯的麻醉作用及对心血管系统的毒性较乙烯强。丙烯的慢性影响与乙烯相似。Harmful to environment, water, soil and atmosphere. Harmful to heart and blood vessel. More toxic than C_2H_4.

（9）高氯酸锂

$LiClO_4$，吸入、食入引起健康危害：本品对眼睛、皮肤、粘膜和上呼吸道刺激性。危险特性：强氧化剂。 Hazard: strong oxidant. Thill to eye, skin, breath.

（10）N-甲基-2-吡咯烷酮

C_5H_9NO，本品属微毒品，燃性危险特性：易燃液体，遇明火、高温、强氧化剂可燃；受热分解有毒氧化氮气体。Flammability, to decomposed to toxic NO_X.

（11）磷化氢

PH_3，有芥子气味极毒气体。含有少量二磷化氢。在空气中自行燃烧而发光，生成五氧化二磷和水。毒剂。Terribly toxic gas.

（12）砷化氢

AsH_3，毒剂。Terribly toxic gas.

（13）五氧化二磷

P_2O_5，对皮肤有腐蚀性。极易吸收空气中的水分。能溶于水，放出大量的热，先形成偏磷酸，后变成正磷酸。Causticity to skin, sensitive to moisture.

（14）甲醛

HCHO，高毒化学品，是无色、具有强烈气味的刺激性气体，High toxic compound.

6 Emergency Response and Rescure

6 Emergency Response and Rescure

6.1 What have been done

（1）采用安全性高的正极材料、低毒电解质盐、添加电解液阻燃剂等。

Adopt high safe anode electrode materials, low toxic electrolytes, additives to block burn.

（2）优化电池内部结构、安全阀及过充保护控制电路和新材料设计，采取相变材料（PCM）进行热管理，对每个单体电池均能进行实时智能控制，增强安全性能.

Optimize battery internal structure, safety valve, overcharge proctect and new materials, smart control to every cell, to increase safety.

（3）避免撞击、曝晒、雨淋和外部短路，不在高温和充电状态下使用，养成良好的使用习惯。

Avoid raming, strong sun shine, rain and external short-circuit, high temperature and charge state using.

以上工业的现有安全措施只能算是预防的初级阶段，对安全事故发生后的有毒有害影响无能为力。 **However, the above steps have no help for the toxic gases leakage and burst accidents.**

（1）事故危害及急救措施 Accident's damage and rescure steps

锂动力电池发生电解液泄漏、冒烟起火、爆炸事故，吸入、或经皮吸收泄漏的电解液或燃烧产生的毒烟，均可对人体和环境造成损害。 皮肤组织接触后可对皮肤产生腐蚀作用，形成灼伤、腐蚀、坏死、溃疡。浓烟中含有多种有毒物，如HF、LiF等，人体吸入后，对肺组织产生剧烈的刺激和腐蚀作用，使肺泡和毛细血管通透性增加，而导致肺水肿。

When EV Li-ion battery happened electrolyte leakage, toxic smoke, fire, burst accidents, personal injury would be resulted in breathing or skin adsorption toxic smoke from the burning, environment damage would be formed. The smother contained many kinds of toxic matters, such as HF,LiF, could produce strong stimulation and cauterization to lung.

皮肤或眼睛接触 Skin or eye touch

吸入 Inbreath

（2）事故处置 Treatment

火灾 Fire

泄漏电解液通常含有强氧化性，能与多种物质如金属粉末、纤维素、木屑、棉花、废纱头等接触反应引起燃烧，甚至发生爆炸，并散发出有毒烟雾。

The leaked electrolyte often has strong oxidation, can react with many matters such as metal powder,fibrin, timber, cotton, thrum and so on to cause burning, burst and to disperse toxic smother.

在灭火过程中建议做下列处理：Treament in fire extinquish

（a）如有可能，转移未着火的容器。防止电池包装破损，引起环境污染。Divide the unfired parts, defend the package, defend environment pollution;

（b）消防人员必须穿全身耐酸碱消防服，佩戴自给式呼吸器，在上风向隐蔽处灭火。The fireman must wear acid-alkali-resistant protection dress, wear self-support breath mask, extinquit fire windward.

（c）用水灭火，同时喷水冷却暴露于火场中的容器，保护现场应急处理人员。

（d）收容消防废水，防止流入水体、排洪沟等限制性空间。 Collectand prevent the waste water flow into river, flood channel limited space.

（e）消防废水稀释处理后排入废水系统。

水上泄漏 Leakage in water

(a) 建立警戒区 Certainfy the alertness zoon

(b) 控制泄漏源 Control the leakage source

(c) 收容泄漏物 Collect the leaked matters

陆上泄漏 Leakage in land

(a) 建立警戒区 Certainfy the alertness zoon

(b) 控制泄漏源 Control the leakage source

(c) 收容泄漏物 Collect the leaked matters

（3）应急预案内容 Emergency pre-cases

应急指挥机构 Command organization

成立事故应急救援领导小组，下设紧急操作组、应急专业组、消防救援组、物资保障组、后勤医疗保障组、保安救援组、通讯保障组等，以上统称“事故应急小组”。

应急救援程序 Emergency rescure procedures

（a）应急救援领导小组成员接到报告后，应立即赶赴现场，并同时指挥专业组进场待命。如有人员受伤，应先带防毒面具进入电动汽车将人员紧急救出，由后勤医疗组治疗；如着火，应通知消防队进场灭火。
（b）指挥疏散现场无关人员，设立警戒隔离带。
（c）灭火后，应立即组织进行事故现场的隔离和保护。
（d）组织检查事故设备情况，确认车辆、电池损坏程度。
（e）应急处理和救援终止后，恢复应急处理和救援人员的正常生活工作次序。
（f）组织进行事故的调查分析，制定落实防范措施，确保在运锂动力电池的安全运行。

事故的预防 Defense for safety accident

（a）动力电池空间保持适宜的温度和湿度，并保持通风；**The battery chamber keep fitting humidity and temprature, keep ventilation.**
（b）驾驶员出行前应对电池进行巡视，检查壳体是否异常、阀门等是否堵死等，发现问题及时联系处理；**The driver should check battery before driving, shell ,valve, any question contact the repairman.**
（c）按规程定期进行电池的性能进行检测，加强对电池的维护，保证设备设施的正常运行，发现异常应及时更换。**Good maintenance.**
（d）车配灭火器、防毒面具；Equip fire extinguish, defense mask.
（e）每年验车、每半年验电池，进行一次通信设备、消防报警系统、逃生警报系统等的检查维护，并形成记录。Check battery twice a year. Check alarm system,escape system once ayear.

Conclusion

锂动力电池成为世界各大汽车公司的首选竞争电池，锂电池电动汽车已成为未来城市交通的一个重要发展趋势。但随着电动车的快速发展，动力锂电池的用量将会逐年成倍增加，动力电池带给环境的压力也会越来越大，对城市的环境保护又提出了迫切需要解决的新问题。因此，应尽快开展动力锂离子电池有毒有害物质的谱系、安全与应急防护研究，以应对交通事故中剧烈碰撞和高温导致电池泄露、爆炸、燃烧时释放大量有毒有害物质的紧急状况，制定锂动力电池车遭遇事故的处理预案，指导大量废弃锂离子电池的回收和综合处理工作，防止锂离子电池污染环境，保护人民身体健康。

With the quickly development of EV, the quantity of EV Li-ion battery will increase geminationly, the pressure to environment will increase respectively, new and emergent problems arosed and cry for resolution, to answer the EV battery's leakage, burst, fire and much toxic matters.

To constitute pre casees, direct the abandon battery's recycle and tranment, defend the Li-ion battery's environment pollution, protect people's in good health condition