

Recycling of Advanced Batteries for Electric Vehicles

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Abstract

The pace of development and fielding of electric vehicles is briefly described and the principal advanced battery chemistries expected to be used in the EV application are identified as Ni/MH in the near term and Li-ion/Li-polymer in the intermediate to long term. The status of recycling process development is reviewed for each of the two chemistries and future research needs are discussed.

Introduction

Although electric vehicles have existed since the late 19th century, they largely fell out of favor with the improvement of the internal combustion engine and low prices for its associated fuels. With the oil crisis of the 1970s, interest in alternative fueled vehicles, including electrics underwent resurgence and serious development efforts reappeared. These efforts were difficult to sustain as oil prices fluctuated and only small numbers of conversion vehicles were produced. In the early 1990s, regulatory issues emerged as a major driving factor with the California Zero Emission Vehicle (ZEV) initiative. The United States Advanced Battery Consortium (USABC) and more recently the Partnership for a New Generation of Vehicles (PNGV) were formed to address technical needs for commercially viable electric and hybrid electric vehicles. These groups receive active participation by the major manufacturers of automobiles in the U.S. and limited numbers of modern EV designs are being offered to consumers in certain areas (e.g. under MOU agreements with California) as a result. The limited range of EVs, particularly with the lead-acid batteries that were initially the only option available, has been viewed as a major impediment to wide scale commercialization. Therefore much research has been and continues to be directed toward advanced batteries, other energy storage devices (capacitors, flywheels), fuel cells, and hybrid power plant designs.

The US Department of Energy, which is also a major participant in the USABC and PNGV, has been working to address infrastructure barriers to the commercial acceptance of EVs since the early 1990s. As an outgrowth of a workshop held in early 1991 on sodium-beta batteries¹, a working group was established to identify and recommend solutions to barriers in the areas of battery shipping, battery reclamation/recycle, and in-vehicle safety. The Advanced Battery Readiness Ad Hoc Working Group, as it is now known, continues to provide a forum for discussion of these issues. Much of the information in this paper is derived from meetings of the Reclamation/Recycle Sub-Working Group section. The expressed goal of this Sub-Working Group is to ensure that

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cost effective means exist for the collection and reclamation/recycle of electric vehicle batteries at end-of-life.

Generic Issues in EV Battery Recycling

Several generic issues have been identified during discussions of potential recycling processes for EV batteries. These are not specific to particular battery chemistries, and may appear to varying degrees depending on other uses and markets for the materials involved. The EV battery market is potentially very large in numbers and each battery is also relatively large in capacity, so that the amount of material that could eventually be available for recycling is also large. This has consequences for the choice of recycled product and on whether it would be preferred to sell materials on the open market or use them strictly for new battery production. If the existing market for a recycled material is small compared to the amount that would be generated from recycled EV batteries, a collapse in the price may occur or it might not be possible to sell the reclaimed material at all.

If the existing market supply is much larger than what would be generated from EV batteries, the price will be relatively insensitive, but also low. Materials with high prices tend to have limited markets while those with low unit prices tend to be produced in very high volumes. This can be illustrated using curves called exclusion charts³, which show a certain price level is "excluded" at a given production volume. The amount of material available to reclaim or recycle from EV batteries at a given point in time has also been difficult to predict. Small amounts of scrap from prototype battery production are typically not of interest to processors that have a recycling or reclamation process already running and the amounts are also too small to support a dedicated recycling facility. Larger amounts of material will become available as production ramps up, but the rate of increase and the life of product in the field are uncertain, at best, in the early stages of development. The smaller size of the batteries needed for the hybrid vehicle application has likely made recyclers more reluctant to invest in process development until a threshold volume is reached for the waste stream.

Another generic concern is that the development, licensing and full scale implementation of a new battery recycling process could take as much as 10 years². The time for approval of permits is particularly unpredictable and could be several years in itself. This motivates the use of preexisting recycling facilities that are already permitted and built and reduces the dependence of the recycler on a single waste stream during the early stages of commercialization. However, the drawback to this approach is that it is unlikely that such a facility would be able to carry out a comprehensive recycling operation on an advanced battery chemistry.

Advanced Battery Chemistries Likely to be Found in EVs

The growth in the population of EVs in the past few years has continued to be measured. With the modification of the California program from mandates to memoranda of

agreement (MOAs), and the court decision that other states cannot implement ZEV programs that are more restrictive than that of California, the number of EVs has remained well below the 10% level envisioned in the original plan for 2003. Hybrid electric vehicles have begun to appear in the mix, and both Toyota and Honda have announced plans to introduce hybrids on the US market during the next year.

In the 1997 time frame, a significant number of automakers were still using lead-acid batteries in EVs. Nickel/Metal hydride batteries were the most prevalent advanced battery system and lithium-ion was undergoing limited tests but was not widely available⁴. Today, the nickel/metal hydride battery has increased in popularity and is now the standard energy storage unit in the EV1. It is also the battery system proposed for the Toyota and Honda hybrid electric vehicles. Use of Li-ion batteries in EVs has not expanded significantly, although the high energy density of the lithium systems continues to be of interest for pure electric vehicles. What will happen in the long run with hybrid vehicles is very uncertain at this point. Systems such as sodium/nickel chloride are still being made, but there are no known plans to introduce them on the mass market in the near future. Therefore, the best prospects for implementation in the near term seem to reside with nickel/metal hydride. Lithium-ion or perhaps lithium-polymer are possible options that offer better performance with lower weight, assuming questions regarding safety and life expectancy can be resolved satisfactorily. The status of recycling for these two battery classes will be discussed in more detail below.

Ni/MH Battery Recycling Status and Future Needs

Ni/MH batteries can be partially reclaimed today through pyrometallurgical processing, although the process most commonly used is focused entirely on the nickel, chromium and iron fraction. Rare earths and other metals contained in the hydride alloy are not separated and end up in the slag, which is eventually sold as aggregate for road construction. The principal facility of this type in the US that accepts Ni/MH battery waste is operated by the International Metals Reclamation Company (INMETCO). A variety of wastes from the stainless steel industry are processed in rotary hearth and electric arc furnaces by INMETCO to produce a standard remelt alloy that can be reused by stainless steel producers. Ni/MH batteries work well in the INMETCO process due to their high content of nickel and iron and since batteries are only a fraction of the waste stream being processed, the amount of battery waste that is available is not so important. At present levels of waste generation, there is no fee levied to process Ni/MH scrap, but there is no profit, either.

Laboratory studies have been conducted on hydrometallurgical methods for processing Ni/MH batteries. Hydrometallurgical treatment provides metal salts as products, which may offer market advantages in certain circumstances compared to the primary metals produced by smelting. Another advantage is that the separation and recovery of other valuable constituents such as titanium, vanadium, zirconium, and rare earths may become possible. The U.S. Bureau of Mines (USBM) conducted exploratory research on hydrometallurgical processing options for several years^{5,6}, concluding that these options

are indeed feasible for battery scrap containing either AB₂ or AB₅ hydride alloys. AB₂ metal hydride electrodes typically contain about 54% Ni + Co, 42% Ti + V+Zr, and 4% other elements (Al, Cr) by weight. The AB₅ electrode consists of a LaNi₅ type alloy on a nickel substrate. The alloy contains about 33% rare earths, 10% Co, 50% Ni, 0.12% Fe and 6% other metals (Mn, Al). USBM evaluated several different leaching protocols and acid solutions for extraction efficiency on whole batteries, cracked batteries, and components. A two-stage leaching process was found to be particularly effective for concentrating the Ti, V, Zr, and Cr species in solution. Preliminary precipitation tests to recover partially separated metals from solution were run using pH adjustment, carbonate precipitation or oxalate precipitation, although the optimum methods for producing the highest purity products were not determined. Nickel and cobalt could be recovered by electrowinning or solvent extraction as well as by precipitation techniques.

An analysis of the operating revenue that could be generated from chemical separation and physical/chemical separation processes for recycling Ni/MH batteries was compared to the pyrometallurgical process in a report to NREL⁷. Revenues (costs) were estimated for both AB₂ and AB₅ hydride alloy battery designs. Other general assumptions in the cost calculations were that a plant was sited in California and was processing 30,000 metric tons of EV batteries per year. The chemical process is based on an acid leach of the battery materials, followed by precipitation of all but the nickel and cobalt. Nickel and cobalt are recovered by electrowinning. The major products recovered are nickel-iron scrap, steel scrap, polypropylene and nickel metal. In the physical/chemical separation process, the battery electrodes are physically separated prior to chemical processing and the metal hydride alloy powder is recovered and returned to hydride alloy producers. The rest of the procedure is very similar to the chemical process. For the pyrometallurgical process, all of the battery electrodes and powders are smelted to form a ferronickel product and slag, which is enriched in hydride alloy constituents. Slag from batteries containing AB₂ alloy could be smelted further to produce ferrovanadium while rare earth producers may be interested in the enriched rare earth content of the slag from AB₅ batteries. The only other products are steel scrap and a very low-grade furnace slag.

In the most favorable case (physical separation/chemical process), the revenue from the recycling process was predicted to be between \$5.43 per kWh for the AB₅ alloy and \$6.01 per kWh for the AB₂ alloy. This is largely due to the value of the credit that can be obtained for the physically separated hydride alloy scrap, although the process is still predicted to generate revenue without it. The revenue of \$3.09 per kWh from the chemical process is second best for the AB₅ alloy and the pyrometallurgical process comes in third at \$1.35 per kWh. For the AB₂ alloy, the pyrometallurgical process looks better at \$2.45 per kWh and the chemical process does not generate revenue at -\$0.16 per kWh. The better cost performance of the chemical process in the case of the AB₅ alloy is a result of both somewhat lower processing costs and a significantly higher product credit due to the cobalt content.

Little follow on evaluation has occurred for Ni/MH battery recycling processes since the studies above were completed about 1994⁸ in spite of the potential benefits that have been

shown. Optimization of the hydrometallurgical type processes is not nearly complete and feasibility and pilot scale up experiments must also still be done. Two factors that seem to be contributing to the low level of interest are the current low prices in the primary metals market and the slow increase in the number of fielded EV batteries. Operators of existing commercial smelting operations are unwilling to bother with small, infrequent shipments of battery manufacturing scrap and returns of end-of-life batteries from the field are still miniscule. Even waste processors, such as INMETCO, which are willing to accept small waste shipments, will not pay for the scrap at the current level of volume and price. Research on improved, more comprehensive recycling processes is not occurring because profits in the near term will be too low to justify the investment. However, the relatively high cost of the Ni/MH battery system makes it important to maximize the recycling credit that is obtained and this will only happen with the development of a more comprehensive recycling process.

Lithium-Ion Battery Recycling Status and Future Needs

Recycling capabilities for lithium batteries have advanced significantly since the early 1990s. Initial methods focused mainly on deactivation and safe disposal rather than material recovery due to the prevalence and well known reactivity of lithium metal in the primary batteries that made up the bulk of the commercial product^{9,10} at that time. The tremendous growth in the rechargeable lithium battery area has stimulated efforts to at least reclaim the most valuable components of lithium-ion cells and progress has also been made in finding ways to reuse the lithium salts that can be recovered. Although EV size Li-ion battery modules have not been fielded in significant numbers, opportunities to dispose of very large lithium primary batteries have required development of handling techniques that will be useful for EV battery modules.

The leader in commercializing the lithium-ion battery technology was Sony and they are also the only Li-ion battery manufacturer to develop a recycling process¹¹. Production of Li-ion batteries by Sony began in 1991 and a battery-recycling project began the next year in conjunction with Sumitomo Metals and Mining Co., Ltd. The Sony Li-ion cell contains a LiCoO_2 cathode and cobalt comprises 15-20% of the battery weight. Since cobalt is a relatively expensive material compared to the other battery constituents, its recovery is the primary objective in the recycling process. Besides the cobalt, which is recovered as cobalt chloride, iron and copper are also recycled from the used Li-ion cells, but the lithium is not reclaimed. If the cathode is changed to a Ni material at some point, the same recycling process will continue to be used.

Toxco has developed processes to recover lithium as lithium carbonate from lithium batteries and other types of lithium-containing wastes¹². As much as 98% of the available lithium can be recovered, along with a similar fraction of the available cobalt and much of the Al, Fe, and Ni. The lithium carbonate can be returned to lithium production and Pacific Lithium, Ltd has done this. More recently, Toxco has set up its own facility to convert the lithium carbonate back into electrolyte salts for lithium batteries. Clearly, it is

feasible and profitable to recycle the cobalt cathode and lithium components of these batteries.

Recycling of the more valuable constituents of Li-ion EV battery modules should follow in a straightforward manner using the processes developed on the strength of the rapidly growing market for the smaller Li-ion batteries in portable electronics devices. A preview of the handling constraints that will be posed by the larger EV modules has been obtained from work to dispose of 4500 large primary lithium/thionyl chloride cells¹³. These 570-pound batteries are sliced open under cryogenic conditions in order to reduce reactivity enough to safely control the recovery of deactivated lithium salts.

One of the future recycling needs for the lithium-ion battery chemistry involves testing of improved methods for recovering alternative cathode materials. Since the economic incentive to reclaim these materials will be less than for cobalt, it will be important for the processes to be highly efficient and to use cheap reagents. Other opportunities are in recovery of carbon anode materials and most likely processing them back into new battery anodes because this is the most valuable form for this material. This will be a difficult task requiring extensive study before feasibility can be proven. Another area where work is needed is on the lithium-polymer version of these batteries. The use of this battery in EVs is further away than lithium-ion systems and very little testing has been carried out. Lithium-polymer batteries will contain a larger fraction of polymeric materials that have rather unique properties and therefore could be a source of recycling revenue. Cell disassembly methods will also likely need to be reviewed in order to optimize them for what could be unusual battery form factors. Investment in recycling process improvement will continue to be difficult since most of the high value constituents are already accounted for and there are only small numbers of prototype lithium-polymer batteries in the field.

Summary

The types of advanced batteries likely to be used in electric and hybrid electric vehicles has narrowed to Ni/MH in the near term and lithium batteries in the intermediate to long term. Growth in the population of EVs continues to be slow. Whether the introduction of hybrid electrics will accelerate market growth remains to be seen at this point. A pyrometallurgical process exists to recycle Ni/MH batteries, although not all of the hydride alloy metals are recovered in a high value form. More research is needed in this area, but activity on development of more comprehensive recycling methods for the Ni/MH chemistry has actually declined in recent years. This is most likely due to the low prices currently being seen in the primary metals markets as well as the low numbers and slow growth in the EV market. Progress has been made in recovery of cobalt and lithium from lithium-ion batteries, but much more remains to be done. A variety of anode and cathode materials are still being evaluated for use in the lithium-ion battery system, and the uncertainty about the precise set of materials that will be encountered has made the potential developers of recycling processes cautious. The enthusiastic acceptance of Li-ion cells in portable electronics applications is tempered by the realization that fielding of large Li-ion batteries in EVs is not likely to occur in the near term.

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