Presidential Green Chemistry Challenge Awards 2012 Nomination
Zero Emission Production of Green Lithium Ion SuperPolymer® Battery
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Project Title - Unique, Non-Toxic Lithium Ion SuperPolymer(R) Battery Manufacturing

Recent Milestone Electrovaya's Green Chemistry innovation is the development of a non-NMP (and hence non-toxic) manufacturing process for Lithium Ion batteries (over 20 US Patents awarded or applied for). Its recent application, in partnership with Chrysler, in Chrysler's RAM truck plug-in hybrid electric vehicle and Minivan plug-in hybrid electric vehicle is an important milestone in clean transportation and advanced battery technology.

Eligibility - Electrovaya's technology is eligible for the small business award. It also fits into award groups (2) use of greener reaction conditions and (3) design of greener chemicals.

US Component - Chrysler Group LLC., working out of Auburn Hills, Michigan, with Electrovaya, working out of Malta, New York as the battery supplier have together performed systems-level research and development for the design of its plug-in hybrid versions for the RAM truck and Minivan platforms. A demonstration fleet of both the RAM truck and Minivan plug-in hybrids, featuring Electrovaya's Lithium Ion SuperPolymer battery packs, is currently being deployed in cities throughout the nation. This represents the first plug-in hybrid electric versions of trucks and minivans worldwide by a major OEM.

Abstract: Conventional Lithium Ion Cell production is environmentally polluting. The electrode manufacturing process uses large quantities of the toxic solvent NMP (n-methyl pyrrolidone) which is now suspected to cause birth defects and is listed as such by the Environmental Agencies in California, Japan, EU and elsewhere. During manufacturing of the lithium ion electrodes, toxic NMP solvent is used for electrode coating, which then subsequently has to be removed through a long furnace (occasionally 100 meters long) where the NMP is slowly evaporated off. Recovery of the toxic NMP is then attempted and some NMP escapes. The lithium ion cell and battery business is today a multi-billion dollar industry. Toxic NMP based lithium ion battery plants are a global problem. In addition to the environmental concerns, the use of large quantities of toxic solvents in manufacturing leads to high capital equipment costs, increased operating costs and uncertain future liability costs.

Electrovaya's cells are produced using a unique, non-toxic manufacturing process. The use of toxic solvents, like N-methyl pyrrolidone, is ubiquitous in lithium ion battery production. By eliminating the use of solvents, Electrovaya has not only eliminated the toxic aspect of production, but also eliminated several pieces of very energy-intensive drying and solvent-recovery processes.

Electrovaya's SuperPolymer® batteries address the growing problem of energy generation and storage. Advanced energy storage for in plug in hybrid electric vehicles and e-bikes provides a potential alternative to consumption of non-renewable resources and is well recognized as an important solution to reduce greenhouse gas emissions. Currently, Electrovaya's battery technology is used in a demonstration fleet across the nation of plug-in hybrid electric versions of Chrysler's RAM pickup trucks and Minivan platforms. The same technology is also used in grid energy storage systems, as a solution to the power stability and energy storage problems associated with renewable resources. Energy storage systems are essential in order for

renewables to comprise a significant portion of a grid's energy supply. Electrovaya recently delivered a 1.5MW system to a south-west utility for energy storage use in conjunction with its photovoltaic program.

Overall, Electrovaya's Lithium Ion SuperPolymer(R) battery technology enables the development and commercialization of clean transportation alternatives such as plug-in hybrid electric trucks and minivans. Furthermore, unique clean manufacturing process ensures a much lower environmental footprint with its lower energy intensive process and removal of suspected toxic solvents.

Chemistry

NMP is used in all major manufacturing plants for lithium ion batteries. These plants were initially based in Japan, South Korea and China, however recently NMP based plants are being built in Michigan and elsewhere in the US. Attempts have been made in China to replace the NMP based processing and use other methods such as water. However, the performance of such water based batteries has been poor as any Lithium coming in contact with water forms very stable hydroxides. This is especially true when used for processing of cathodes where lithiated metal oxides or phosphates are used as electrode materials. The Electrovaya Green innovation overcomes this problem.

At a fundamental level, Electrovaya's SuperPolymer® batteries utilize the same technology found in all lithium ion cells: the charge transfer occurs by ions, rather than electrons, moving between the electrodes. At the electrodes, the ion undergoes the intercalation process, whereby it is incorporated or removed from the electrode material, without causing a significant structural change. The patented[1] SuperPolymer® battery breakthrough is in its novel nanostructure. This enables more energy to be stored in a smaller space, so applications are smaller, lighter and more powerful. The cell assembly is illustrated in figure 1, below. Figure 2 shows the electrode and separator in greater detail.

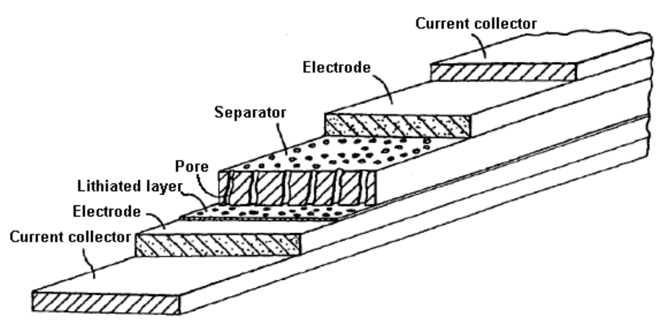

Figure 1: SuperPolymer® cell assembly

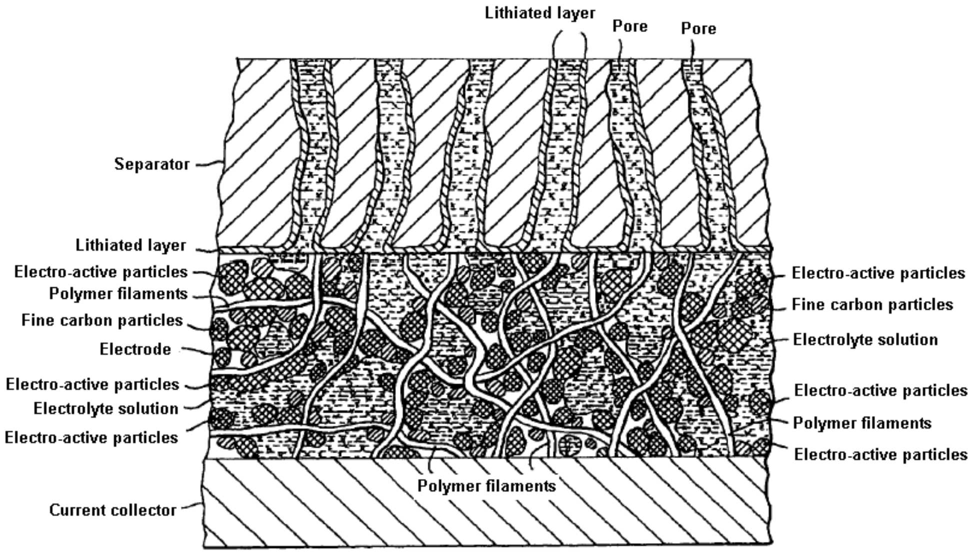

Figure 2: Current collector, electrode and separator

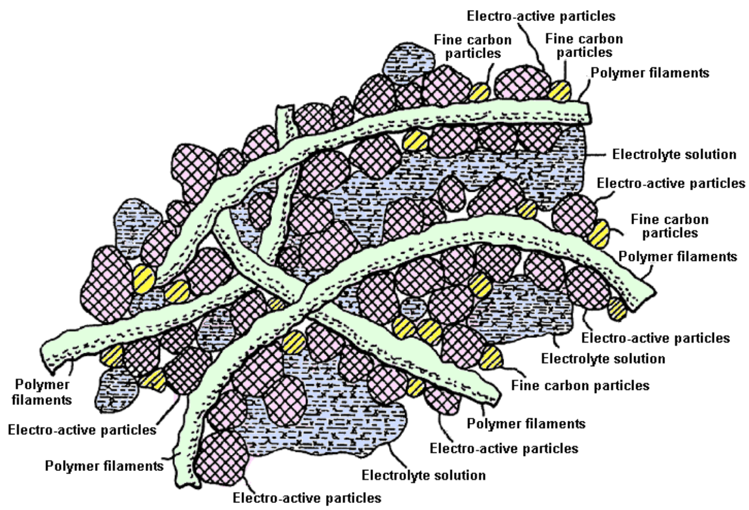

Figure 3: Electrode nanostructure

The electrodes, as seen in figure 3 above, are made of pliable, solid, ion conducting polymer filaments which have adhesive surfaces and electro-active particles adhering to the surfaces. The filaments and the adhering particles form a matted layer having void space which is filled with a non-aqueous, lithium ion compound-containing liquid electrolyte. One of the key advantages of the electrode mixture is that lithium ion movement can occur both via the solid electrolyte filaments and via the liquid electrolyte, thereby enhancing the overall conductivity within the electrodes.

Furthermore, the inert, porous, multi-layered, polymer separator (figure 2) is coated on both faces with a thin (~2µm), solid, ion-conducting polymer layer which in addition partially fills the pores. Note how in figure 2, the lithiated polymer layer between the electrode and the separator extends and coats the walls of the pores within the separator. The thin coating leaves sufficient void space in the pores for an organic lithium compound-containing liquid electrolyte to be added. This electrolyte further facilitates ionic movement and reduces the impedance of the cell.

It is believed that the passage of lithium ions from one electrode to the other may take place by means of the solid, ion conducting polymer filaments and the solid, ion conducting polymer coating carried by the porous separator, as well as by the lithium compound-containing solution held in the void of the matted particulate electrode layer and in the partially filled pores of the separator. Alternatively, the lithium ions may also cross from liquid to solid and vice versa, although the mass-transfer rate through this mechanism would be relatively low.

As mentioned previously, this nanostructure represents a platform technology. Most improvements made in battery technology are slight incremental benefits resulting from slight changes in the exact chemical composition of the electrodes. The SuperPolymer® structure provides an advantage to any lithium ion cell, whether it's $LiCoO_2$, LiV_2O_5, $LiMnO_2$, etc. With slight materials modifications, the design could potentially be applied not only to lithium ion batteries, but also to any other type of ion battery. By providing a faster, more efficient transport of ions, SuperPolymer® cells achieve higher energy and power densities.

Green Manufacturing

Virtually all major battery manufacturing uses toxic solvents, most commonly N-methyl pyrrolidone (NMP). In Europe, NMP must be labeled as toxic and potentially harmful to unborn children[2]. In 2006 the California Department of Health Services issued a health hazard advisory on NMP[3]. SuperPolymer® cells are manufactured without the use of NMP or other toxic solvents, creating a greener battery life cycle.

Not only is the toxic component eliminated, but the need for solvent drying and recycling too, so several energy-intensive operations can be also removed. One life cycle assessment[4] modeled plug-in hybrid electric vehicle (PHEV) batteries made with and without NMP. NMP batteries were estimated to produce 25% more CO_2 equivalent across their lifecycle, as shown in figure 4 below. Because lithium-ion batteries are relatively new, recycling has not yet been studied extensively, but SuperPolymer® cells would not vary significantly from other lithium-ion batteries in this regard.

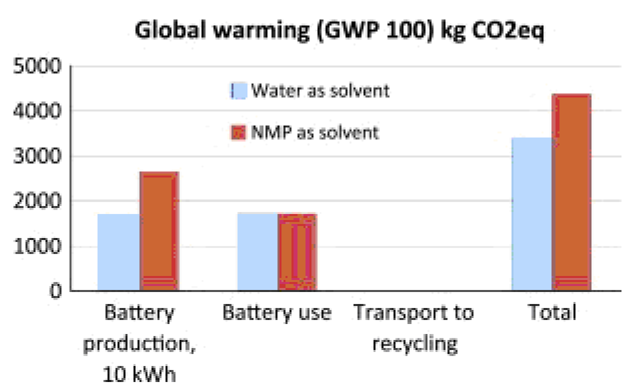

Figure 4: Estimated global warming potential across life cycle for a 10kWh PHEV lithium ion battery[4]

Application – Clean Transportation

With the number of cars on the road growing every year, transportation is becoming an ever larger environmental problem. Use of petrochemicals in internal combustion engines (ICEs) has resulted in high greenhouse gas emissions, poor air quality, and ecological damage at extraction sites. SuperPolymer® batteries can be used to replace or supplement ICEs, potentially eliminating the need for fossil fuel consumption.

Depending on the source of the electricity stored in the battery, vehicle operation has the potential to be emission-free. Of course, if the electricity had been supplied by a fossil-fuel power plant, the overall emissions would be more similar to an ICE. However, even in this case the battery still offers an advantage – electricity generation, and thus pollution, would be decoupled from use. So while a million ICE cars clustered together in a city create a human health hazard, a million electric cars in that same city can be electrified by a power plant far away from the city, where the pollution will not affect nearly as many people.

Chrysler has produced a demonstration fleet of 140 Ram 1500 PHEV pickup trucks, currently being tested in cities across the nation, which use SuperPolymer® batteries. Initial estimates suggested a 65% improvement in fuel economy, and the vehicle boasts a 20 mile zero-emission, pure-electric range.

Application – Grid Storage

The most popular renewable energy sources, unfortunately, are intermittent energy sources. Wind and solar tend to produce either too much or too little power at any given time, which changes the frequency of the alternating current (AC) in the grid and causes stabilization problems. Lithium ion batteries can charge and discharge rapidly – if the sun dips behind a cloud, the battery can almost instantaneously replace a solar panel in supplying a certain amount of power to the grid. This keeps fluctuations in AC frequency to a minimum and maintains grid stability. This would be considered a *power* application because it deals with energy in very small timeframes, i.e. the battery may switch between charging and discharging several times in one minute.

Lithium ion batteries, especially SuperPolymer® batteries, have a high energy density and so are also well suited for storing large amounts of energy for longer periods of time. This allows them to store power generated throughout most of the day, and then supply that power during the few hours when demand is at its peak, in a process known as “peak shaving”. Peak-shaving not only allows surplus energy from renewables to be saved for when it’s needed, but also allows fossil-fuel plants to operate more efficiently by working at constant-output, reducing fuel waste. Peak-shaving would be considered an *energy* application, because it deals with large amounts of energy being supplied over relatively long timeframes.

The unique nanostructure of SuperPolymer® battery cells allows them to not only store large amounts of energy, but to discharge that energy rapidly. While most battery cells and other types of energy storage systems excel in one area and perform poorly in the other, SuperPolymer® cells are ideal for both power and energy applications. By stabilizing the grid and providing peak shaving, the batteries allow a significant portion of a grid’s energy to come from solar and wind energy, moving the world one step closer to zero-emission energy generation/distribution.

Electrovaya recently delivered a 1.5MWh storage system made of SuperPolymer® batteries to a major south-west utility for use with its solar power program.

Comparison with Other Technologies

As noted in the previous discussion of chemistry, SuperPolymer® cells have a very high energy density. This allows them to be smaller and lighter than other cells for a given energy capacity. Smaller, lighter cells and be produced, packaged and shipped with less energy and material consumption. In a hybrid vehicle, the weight of the battery has a significant impact on fuel consumption. Figure 5 below shows a comparison between different battery technologies.

Electrovaya's Lithium Ion SuperPolymer® batteries are based on a nanostructured lithiated manganese oxide material. The cells are characterized by their proprietary unique structure: a current collector, adjacent to a negative particulate electrode containing lithiated polymer electrolyte filaments, which in turn is adjacent to a lithiated polymer separator, which in turn is adjacent to a positive particulate electrode containing lithiated polymer electrolyte filaments, adjacent to another current collector. This unique structure provides a faster, more efficient transport of lithium, providing superior energy and power density.

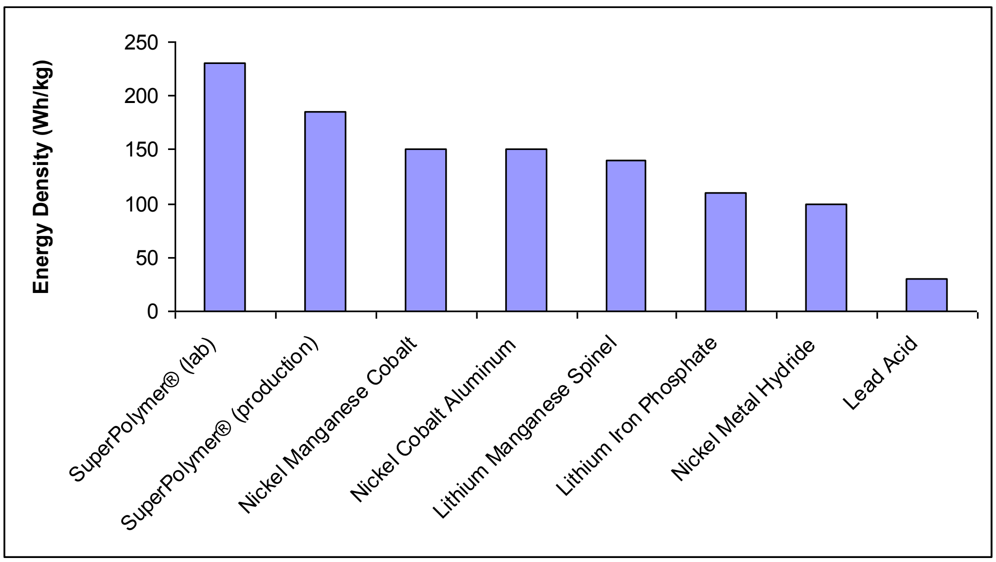

Figure 5: Energy density of different Lithium Ion battery types

In vehicles and transportation, batteries compete with fuels cells, and alternative and conventional fuels. Unlike vehicles that rely on fuel cells, electric vehicles do not require large changes in infrastructure, as almost everyone has access to electrical outlets at home and work, while hydrogen or methane fueling stations are rare. And unlike other alternatives, electric vehicles do not contain large quantities of flammable liquids, and pose much less fire-related risk.

For grid storage options, batteries compete with flywheels, supercapacitors, fuel cells, and pumped hydro, among others. Batteries are unique in that they can be used for short term power applications, or long term energy applications, while other technologies are usually only suitable for one of the two. Flywheels have a low energy density and large standby losses.

Supercapacitors, while highly energy efficient, have a low energy density, are expensive, and require complicated electronics to ensure uniform voltage output. Fuel cells have the advantage of near-instantaneous recharging, but require transport, storage and handling of highly flammable fluids. Pumped hydro is only practical in areas with specific geography, and has an inherent delay after a request before power is supplied. For a system requiring high energy density and some temporal versatility, batteries are the most attractive option.

Summary

Electrovaya's SuperPolymer® batteries are an original, innovative electrochemical technology. They are manufactured using a novel process which eliminates toxic solvents along with the most energy-intensive processing steps, generating less CO_2 equivalent than comparable batteries. Use of Lithium Ion SuperPolymer® batteries in vehicles can drastically reduce emissions. SuperPolymer® batteries are also an excellent option for grid energy storage, which is essential for increasing the portion of energy supplied by wind and solar power. By decreasing reliance on fossil fuels, advanced batteries enable the development and commercialization of clean transportation alternatives such as plug-in hybrid electric trucks and minivans. Furthermore, unique clean manufacturing process ensures a much lower environmental footprint with its lower energy intensive process and removal of toxic solvents.

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4. Mats Zackrisson, Lars Avellán, Jessica Orlenius, Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles – Critical issues. Journal of Cleaner Production, Volume 18, Issue 15, November 2010.
5. Rationale for Reporting List of Chemicals of High Concern to Children Prepared by the Washington State Department of Health for the Children's Safe Product Act – 4/18/2011
6. CAS 872-50-4
7. Substance name 1-Methyl-2-pyrrolidinon (also called N-methylpyrrolidone or NMP)
8. Toxicity
9. N-Methylpyrrolidone is listed by the state of California and the European Union as a developmental toxicant.1,2 In animal studies it caused reduced fetal and birth weights, developmental delays and impairment of cognitive skills in offspring.1,3,4
10. Exposure
11. 1-Methyl-2-pyrrolidinon is used as an industrial solvent for resins, paint strippers, and plastics in the semiconductor industry. It is also used as a finishing agent in textiles, as a pigment dispersant, and as a spinning agent for polyvinyl chloride.1,3,5 It is listed as an ingredient under the synonym (methyl pyrrolidone) in a nail polish remover and five mascaras in an online cosmetic database.6 The Danish EPA detected 1-methyl-2-pyrrolidinon in the coatings of children's wooden toys.7

Other sources:

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