The long, winding road to advanced batteries for electric cars

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(Phys.org) -- Batteries have come a long way since Alessandro Volta first discovered in 1800 that two unlike metals, when separated by an acidic solution, could produce an electric current. In their evolution, batteries have taken on various forms, ranging from lead-acid, to nickel-metal hydride, to current-day lithium-ion.

Now technological advances in batteries are more critical than ever.

Coupled with the alarming rate at which we are exploiting fossil fuels, the world's growing energy demand necessitates that we find alternative energy sources.

"Revolutionizing the transportation market by electrification and transforming the energy grid by widespread adoption of renewable energy sources will require innovative new ideas for energy storage," wrote Michael Thackeray, a senior scientist at Argonne National Laboratory and the lead author of a recent review published in *Energy & Environmental Science*. Batteries could provide that energy storage, and transform vehicles from guzzlers of gas into feats of electricity.

With present-day technology, however, electric vehicles cannot compete with internal combustion vehicles. According to the review, "energy densities two and five times greater are required to meet the performance goals of a future generation of plug-in hybrid-electric vehicles (PHEVs) with a 40-80 mile all-electric range, and all-electric vehicles (EVs) with a 300-400 mile range, respectively." To make the leap, scientists will have to find new couplings of battery materials.

A typical battery cell contains two electrodes – a positively-charged cathode and negatively-charged anode – separated by an electrolyte. The earliest cells contained aqueous, or water-based, electrolytes. However, because water decomposes at a relatively low cell voltage (~1.2 volts), these batteries have limited energy densities.

Pioneer developers of batteries included Gaston Planté, who created the lead-acid battery in 1859, and Thomas Edison, who invented the nickel-iron battery in 1901. Edison's passion for electricity, combined with Henry Ford's hunger to make cars, generated much public anticipation of electric cars a century ago. Before long, however, gasoline-powered automobiles stole the spotlight and have ruled the roads ever since.

“Materials and processing costs, performance limitations and the uncertainties of new, insufficiently validated electrochemical couples and materials in a rapidly maturing market are all factors that indicate that progress in lithium-ion battery technology is likely to be incremental rather than exponential,” wrote Thackeray.

In 1989, nickel-metal hydride (NiMH) batteries, descendants of nickel-based batteries like Edison's, recaptured the public’s interest. They were first used successfully as a power assist to save fuel during acceleration in Toyota’s hybrid-electric vehicle, the Prius. However, because of their relatively small size and limited energy density, NiMH batteries cannot power the Prius over an extended range; the vehicle can travel typically two to three miles on a single charge if powered only by electricity.

The oil crisis of the mid-1970s prompted serious efforts to develop non-aqueous batteries. Researchers at the time had just discovered a solid electrolyte ceramic, ‘beta-alumina’, through which sodium ions could be transported rapidly at about 300 °C. This heralded a new generation of high-temperature batteries. Unfortunately, these sodium-based batteries were prone to short circuits and fires, and required burdensome heating and cooling units to operate, which limited their application in vehicles. The early generation of rechargeable lithium batteries, which used metallic lithium as the anode, also suffered from short circuits and fires.

The “eureka” moment for rechargeable lithium batteries came in 1991 with Sony’s development of a battery for portable electronics. Instead of an anode made of lithium metal, Sony’s battery used a graphite anode that could accommodate lithium, thereby resisting short circuits and reducing the risk of internal heating. It also contained a non-aqueous, liquid electrolyte and a cathode made of lithium cobalt oxide. The battery worked by shuttling lithium ions reversibly between the two electrodes during charge and discharge – giving it the name “lithium ion”.

Lithium is a likely candidate for developing powerful, high-energy batteries. It is the third lightest element and has the highest oxidation potential, or tendency to become ionized, of all known elements. To this day, most Li-ion batteries, such as the ones found in the Chevy Volt (a PHEV) and Nissan Leaf (an EV), still contain a graphitic anode and a lithium metal oxide cathode of some type.

In their present form, Li-ion batteries bear several shortcomings. Continual charging and discharging of the battery wears down the structure and stability of its electrodes. Furthermore, electrolytes of choice contain corrosive and flammable ingredients that are unstable at high voltages, and electrode-electrolyte reactions can degrade electrode stability. To improve the safety and longevity of these batteries, researchers will need to find new electrolytes and ways to protect electrode surfaces at the electrode-electrolyte interface.

Scientists are also looking for electrode materials that can deliver more energy. One option is to develop high-potential cathodes that release large amounts of energy from the battery's electrochemical reactions. These cathodes, however, must be used in combination with electrolytes that are stable at higher voltages.

High-capacity cathodes are another option. They are typically stabilized by manganese ions, which are more stable than other transition metal ions at high voltages. When these cathodes are charged above 4.5 volts, essentially all of the lithium can be removed from their structures. This maximizes the amount of electric charge they can deliver during discharge. However, batteries containing these cathodes are currently limited by electrode and electrolyte damage at high charging voltages.

For anodes, scientists are experimenting with metals and metalloids – such as tin and silicon – that can accommodate significantly more lithium atoms within their structures than a typical graphite anode. The

main problem with tin and silicon is their tendency to expand and contract many-fold during charge and discharge, which shortens the battery's cycle life.

Though new electrode and electrolyte materials can optimize the performance of next-generation Li-ion batteries, they will at best increase energy densities by factors of two or three. That may be enough to satisfy the performance goals of PHEVs, but it falls short of long-term targets for EVs. "Materials and processing costs, performance limitations and the uncertainties of new, insufficiently validated electrochemical couples and materials in a rapidly maturing market are all factors that indicate that progress in lithium-ion battery technology is likely to be incremental rather than exponential," wrote Thackeray.

For exponential increases in energy density, scientists are looking toward Li-oxygen batteries, which contain a metallic lithium anode and an oxygen gas cathode. Though these batteries can potentially pack much more energy, they are plagued with inefficiencies and safety problems in their current form.

Still, researchers are hopeful of a breakthrough. They can now use computing to accelerate the discovery of new electrode and electrolyte systems. This creates a positive feedback loop in which computing informs experiments, and experimental results help refine the computing process. This high-throughput iterative process may be scientists' ultimate hope for discovering materials that can significantly improve the electrochemical performance, safety and cost of batteries.

More information: The paper, Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries, appears in Energy & Environmental Science. Its other authors are Christopher Wolverton (Northwestern University) and Eric Isaacs (Argonne National Laboratory).

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