

# Nanoparticle-based emission catalysts

*A new process more effectively and efficiently prepares automotive catalysts to maximize performance.*

## KEY CONCEPTS:

- Effectiveness of the three-way automotive catalyst is reduced because precious metals tend to migrate along the surface and agglomerate into larger particles.
- A direct-current plasma process has been developed to prepare fine precious metal nanoparticles that range from 2-4 nanometers. This catalyst exhibits superior performance over a longer operating period.
- The nanosized precious metal catalyst can work at a lower treat rate, representing a 50% cost savings in precious metals.

**R**educing automotive emissions increases the need for more effective catalyst technologies. In the U.S., EPA has reduced the NO<sub>x</sub> emission requirements to 1.2 grams per brake hp hour in 2007. This emissions requirement will drop further to 0.2 gram per brake hp hour in 2010.

In a past column, the benefits of a cerium oxide-modified Cu-ZSM-5 catalyst were described in reducing NO<sub>x</sub> emissions.<sup>1</sup> The introduction of cerium oxide enabled the catalyst to function in the temperature range (between 325 C and 350 C) of diesel exhaust. The catalyst can remove 95% to 100% of NO<sub>x</sub> emissions.

The conventional way to reduce emissions in gasoline engines is to use a so-called three-way catalyst that relies primarily on precious metals (palladium, platinum and rhodium). In this approach, the three main pollutants (carbon monoxide, hydrocarbon and NO<sub>x</sub>) are reduced simultaneously. Maximum benefit for the catalyst is obtained by adjustment of the ratio of air to fuel.

For diesel engines, a DOC, or diesel oxidation catalyst, is typically employed consisting primarily of platinum and palladium. Max Biberger, CEO of SDCMaterials Inc., in Tempe, Ariz., says, "Tightening requirements for fuel economy and the use of turbochargers has led to a reduction in the temperature of diesel emissions. This factor increases the challenge in removing pollutants because catalyst performance declines as the temperature drops. Catalyst effectiveness at lower temperatures can only be improved by adding more precious metals which, unfortunately, leads to added cost."

A wet chemical process is the standard currently used for DOC and three-way catalyst fabrication to place precious metals on an oxide surface.

Biberger says, "Use of a wet chemical process is not effective in securing precious metal catalysts on the surface. Due to the wetting angle, the precious metals tend to migrate along the surface, which can lead to agglomeration into larger particles. The result is a loss of catalyst effectiveness."

A process needs to be developed to more effectively and efficiently prepare automotive catalysts in order to maximize performance. Such a process has not been developed until now.

## DC PLASMA

Better utilization of the precious metals is achieved by a patented process for converting the starting materials into nanosized catalysts. Biberger explains, "We have developed a direct-current (DC) plasma process that transforms the precious metal starting materials (typically with particle sizes in the micrometer range) into fine nanoparticles that form the basis for the catalyst."

## The lower treat rate means using 50% fewer precious metals, an annual savings that could be as high as \$4 to \$7 billion.

Biberger indicates that the key to catalyst performance is that the nanosized particles fabricated using this DC plasma methodology do not change their size over a long operating period. He adds, "There is no loss of surface area as the precious metal nanoparticles do not move around and agglomerate."

The nanoparticles derived from the DC plasma range between 2-4 nanometers, which is no different from the conventional wet chemical process. But catalyst prepared by the later procedure are more mobile on the oxide surface leading to agglomeration and loss of surface area.

Biberger says, "We employ a similar ratio of precious metals as compared to conventional processing but can use less catalyst because aging is reduced. The catalyst chemistry also can be adjusted to meet specific applications."

Testing of the catalysts prepared by the DC plasma process was conducted through direct comparison with catalysts used in commercial automobiles. Biberger says, "We have focused on evaluation against catalysts used in Volkswagen automobiles because this car company is the largest manufacturer of light-duty diesel engines and, in our view, has the most advanced technology."

Biberger indicates that his company buys original equipment catalytic converters for Volkswagen cars such as the Golf and the Passat, removes and analyzes the catalyst components and develops a catalyst with comparable properties. Testing is conducted by an independent laboratory. A typical procedure is to test the catalyst for the equivalent of 100,000 miles at a temperature of 800 C and a water concentration of 10% for 16 hours.

The light off temperature ( $T_{50}$ ) for removal of carbon monoxide, hydrocarbons and  $NO_x$  is measured during testing. This parameter is an indication of the temperature at which a catalyst achieves a 50% conversion rate. Biberger adds, "The goal is to build a catalyst with less precious metal

that can convert at lower temperatures over the expected service life."

Figure 1 shows two catalysts developed by the DC plasma technique in comparison to a Volkswagen reference catalyst. The key results for all three emissions categories are shown in yellow. The Volkswagen catalyst exhibits initially lower  $T_{50}$  values, but the  $T_{50}$  figures are much higher when aged.

Biberger figures there is typically 5 grams of precious metal per liter of catalyst in most cars. The DC plasma catalyst can work at a lower treat rate, which will represent a 50% cost savings in precious metals. This could

mean an annual savings of as much as \$4 to \$7 billion.

Looking ahead, Biberger indicates that his company is developing so-called Non-PGM catalysts, or Non-Platinum Group Metal catalysts, i.e., catalysts that contain no precious metals. He figures a commercial, non-PGM product is still a couple of generations away.

On the gasoline side, there is not as much of an incentive to move to new catalyst technologies because precious metal material cost is lower by 50% compared to diesel engines.

Biberger says, "There is only a little room for improving the cost of catalysts used in gasoline engines. However, we are making progress in developing an approach that could be available soon."

Further information on the preparation of diesel engine catalysts using DC plasma technology is found in a recent U.S. Patent Application.<sup>2</sup> Biberger can be reached for additional information at [max.biberger@sdcmaterials.com](mailto:max.biberger@sdcmaterials.com).

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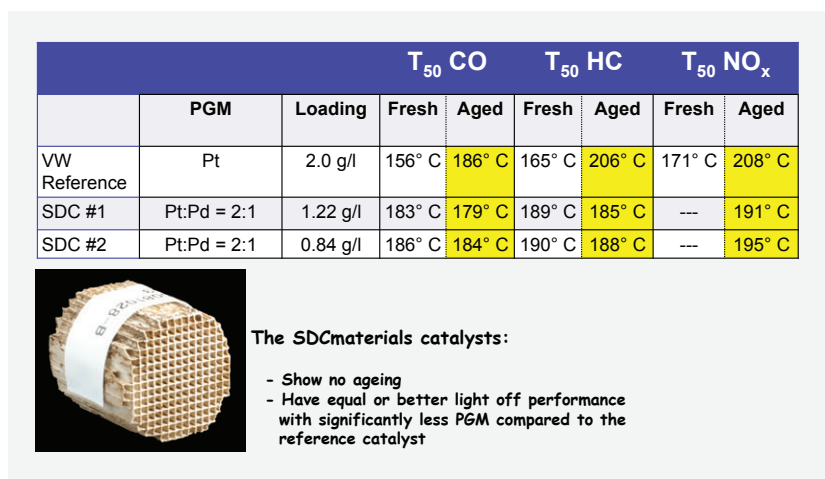


Figure 1 | The light off temperature ( $T_{50}$ ) for removal of carbon monoxide, hydrocarbons and  $NO_x$  is measured for two catalysts developed by the DC plasma technique and compared to a reference Volkswagen catalyst. The lower temperature values for the DC plasma catalysts show that they will operate more cost-effectively over a longer service life. [Courtesy of SDCMaterials, Inc.]

# Layered lithium batteries

*This emerging technology would enable a car to drive 40 miles powered only by a battery.*

## KEY CONCEPTS:

- **Lithium-ion batteries exhibit superior energy-to-weight ratios and slower loss of discharge compared to other battery types. But they do not cycle at a fast enough rate, and there are concerns about their safety.**
- **A transitional lithium battery cathode has been developed that contains a high concentration of nickel ions in the core, which generate high energy but are thermodynamically unstable. In moving away from the core, nickel ions are gradually replaced by more stable manganese ions.**
- **This transitional cathode material improves the possibility of developing an automobile that can be driven for 40 miles just on a battery without recharging. In the U.S., 78% of the commuting is done within this range.**

**T**he high price of oil continues to spur interest in the development of alternative energy sources. One such option is lithium batteries for automotive applications that can provide high performance and better durability over a longer operating life.

An attractive strategy is to develop batteries for use in plug-in hybrid electric vehicles (PHEV). This car combines an electric battery with a small combustion engine to maximize performance, both in driving short and long distances. In the U.S., there is a goal to have more than a million PHEV on the road by 2015. The convenience aspect of this approach is that the consumer would recharge a depleted battery by plugging it into the readily accessible electric grid.

Difficulty has been encountered in developing the right type of battery for this application. Lithium-ion batteries exhibit superior energy-to-weight ratios and slower charge loss than other battery types. But they generally do not cycle (charge and discharge) at a fast enough rate, and there are concerns about their safe use. These issues have prompted the automotive industry to rely upon nickel-metal hydrides.

In a past column, work on preparing a well-ordered lithium nickel manganese oxide was described.<sup>1</sup> This cathode has the potential to exhibit higher energy density and more rapid cycling.

Dr. Khalil Amine, senior scientist and manager of the Battery Technology Group at Argonne National Laboratories, in Argonne, Ill., says, "The two types of PHEV currently under development have all-battery ranges of 10 and 40 miles, respectively." In the former case, battery technology can be designed right now, according to Amine, with the only outstanding issues being calendar life, safety and cost performance.

But the latter case is much more challenging. Amine adds, "The 40-mile target is very desirable because 78% of the commuting in the U.S. is done within this mileage range. Unfortunately, no chemistry is currently available that can enable a vehicle to travel for this distance using just the battery based on specifications prepared by a U.S. advanced battery consortium known as USABC."

A big hurdle is meeting all the energy and power requirements within the weight and volume that is acceptable to the automotive industry. Vehicle weight, as we know from current internal combustion engine technology, is a critical factor in determining the fuel economy of a gasoline or diesel engine-powered vehicle. It is no different with batteries.

Amine says, "Current state-of-the art lithium batteries can generate between 160 and 180 watt-hours per kilogram at the cell level. However, for PHEV-40 miles, we need similar energy densities but at the pack level, which is very challenging."

The specifications outlined by USABC require that a lithium-ion battery must exhibit the combination of superior performance, enhanced durability, safety and low cost. Such a battery has not been developed until now.

## TRANSITIONAL COMPOSITION

A group of researchers has developed a battery cathode material that contains a

## 'Replacement of nickel ions with more stable manganese ions in the outer layer of the cathode material can lead to a more stable battery cathode material that still retains high energy characteristics.'

lithium nickel cobalt manganese oxide cathode of variable composition in order to balance high energy and capacity with added safety and durability. Amine explains, "Nickel-rich cathodes have proven to generate high energy but are inherently unstable.

The high concentration of Ni<sup>++</sup> ions is thermodynamically unstable and can lead to a violent reaction with the electrolyte. Replacement of nickel ions with more stable manganese ions in the outer layer of the cathode material can lead to a more stable battery cathode material that still retains high energy characteristics."

The core of the cathode battery material still contains high concentrations of nickel ions. But in moving away from the core towards the surface, the nickel ions are gradually replaced by more stable manganese ions so that the surface is predominantly the latter ion.

This transitional battery cathode material is prepared by a unique co-precipitation process. Amine says, "A nickel manganese hydroxide precursor is initially prepared in a continuously stirred reactor. Added to this precursor is a nickel manganese species that has a high concentration of nickel. As the process continues, the ratio of nickel to manganese is adjusted gradually to higher levels of manganese."

An image of a cathode particle showing its transitional composition is shown in Figure 2. The key to the process is an interface in which the composition gradually changes from the nickel-rich interior to the manganese-rich surface.

Analysis of the cathode particles is conducted by electron-probe X-ray microanalysis and scanning electron microscopy. Amine says, "The size of the cathode particles is between 10-12 microns in diameter."

Evaluation of the battery containing the transitional cathode particle was conducted in a small cell charged to 4.4 volts and cycled at 55 C. In one study, a cell based on the transitional material retained 96% of its capacity after 50 cycles,

while a cell made from a nickel-rich salt retained only 67% of its capacity after the same number of cycles.

Amine believes the transitional battery cathode material has the potential to power an automobile close to the 40-mile targeted figure. He says, "The gradient particle approach improves the possibility that a car can exhibit a mileage range between 25 and 30 miles."

Future work involves attempting

to transfer the technology out of the lab. Amine says, "We are still doing optimization work and need to increase the concentration of the manganese component in the cathode."

A 20-liter reactor is being set up for scale-up of material. Further information on the preparation and analysis of the battery cathode material can be found in a recent article<sup>2</sup> or by contacting Amine at [amine@anl.gov](mailto:amine@anl.gov).

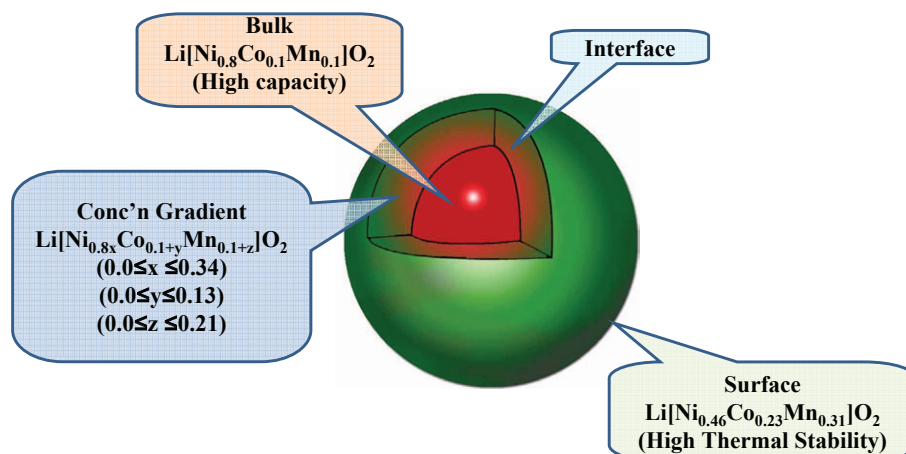


Figure 2 | A transitional cathodic material has been developed that contains a higher concentration of nickel in the core to generate high energy. In moving toward the surface, the nickel is replaced with more stable manganese. This cathode has the potential to be used in a battery, which can power an automobile for 40 miles. [Courtesy of Argonne National Laboratories]

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# Aluminum hydride: Potential hydrogen-storage material

*In addition to automobiles, the new process could be used in superconductors and batteries.*

## KEY CONCEPTS:

- Identification of a suitable hydrogen-storage material continues to be a major challenge because DOE is requiring a system with a mass of 6% hydrogen and a volume of 45 kilograms of hydrogen per cubic meter by 2010.
- Aluminum hydride (alane) has the hydrogen content and volume to meet DOE's requirements but is difficult to manufacture.
- A new electrochemical process conceivably can generate hydrogen from alane for powering an internal combustion engine. The alane can be regenerated through a recycling procedure that improves the efficiency of the process.

**R**esearch is continuing developing more viable ways to store hydrogen for use in fuel cell propulsion systems. Hydrogen by nature is very explosive and difficult to handle. Use of a derivative with a high hydrogen content that has excellent stability is required, particularly because the consumer will need to purchase it in a similar fashion to gasoline.

A past column discussed the preparation and isolation of a series of polyhedral aluminum hydrides.<sup>1</sup> One of the derivatives,  $Al_4H_6$ , has been found to exhibit the best stability and could be a suitable hydrogen-storage material.

The U.S. Department of Energy has a goal of developing a hydrogen-storage system with a mass of 6% hydrogen and a volume of 45 kg of hydrogen per cubic meter by 2010. The objective increases to a system with a mass of 9% hydrogen and a volume of 81 kg per cubic meter by 2015. Aluminum hydride or alane is a potential candidate because it contains 10% hydrogen by weight and has a volume of 149 kg of hydrogen per cubic meter.

Ragay Zidan, advisory scientist at the DOE's Savannah River National Laboratory, says, "Alane is a viable candidate to store hydrogen. Although it is not stable thermodynamically, it is stable kinetically. The hydrogen release from alane is easier than from most other high-capacity hydrogen-storage materials."

But Zidan maintains that the conventional process used to prepare this hydride is impractical. Alane has traditionally been prepared by reaction of lithium alanate with aluminum chloride in diethyl ether solution. The process generates an ether complex of aluminum hydride. Heating under vacuum conditions leads to the isolation of alane.

Zidan comments, "This process has several problems including that it is highly exothermic and people shy away from using diethyl ether as a solvent. The biggest problem is that the byproduct, lithium chloride, acts as an energy sink. An enormous amount of energy needs to be used to melt lithium chloride and electrolyze the melt in order to reverse the process and yield the corresponding metal needed to complete the cycle."

Melting of lithium chloride needs to occur at a temperature above 600 C and requires 429 kilojoules per mole of energy, equivalent to the heat of formation and fusion of the salt to recover the lithium. Direct reaction of aluminum with hydrogen is also impractical because it must be done under high level of hydrogen pressure ( $10^5$  bars) at room temperature.

Development of a more efficient and safer process would potentially enable alane to store hydrogen. Such a process has not been developed until now.

## ELECTROLYSIS

A new approach has been developed to utilize alane as a source of hydrogen and

## This research demonstrates the feasibility of using alane in a reversible process to generate a stable hydrogen derivative suitable as a storage material that can readily release the fuel at the right time.

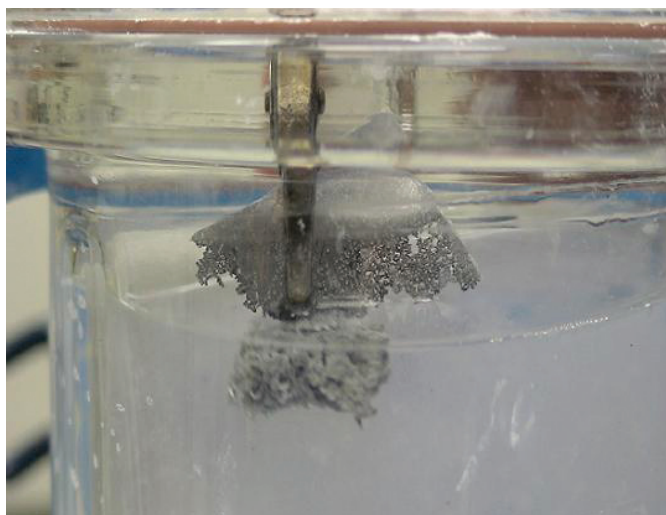


Figure 3 | The electrochemical process for using alane as a source of hydrogen can consume an aluminum electrode. The image on the left shows the aluminum electrode prior to the reaction of the alanate ion in THF. The image on the right shows the aluminum electrode consumed after the reaction. (Courtesy of the Savannah River National Laboratory)

then regenerate it in a cyclical manner. Zidan says, “A breakthrough achieved in 1998 found that the process for preparing sodium aluminum hydride is reversible. We took this information and developed an electrochemical process in which sodium aluminum hydride dissolved in the solvent tetrahydrofuran (THF) is used as the electrolyte.”

The alane adduct with THF is generated at the anode through the reaction of alanate ion ( $\text{AlH}_4^-$ ) with aluminum metal. This can result in the consumption of an aluminum electrode, as shown in Figure 3.

Alane then can release hydrogen using the heat generated in an internal combustion engine to drive the reaction. Concurrently, a sodium cation is reduced at the cathode and can be readily treated with hydrogen gas to form sodium hydride.

Aluminum metal formed in this process is recycled by reaction with sodium hydride in the presence of a titanium catalyst. The result is the regeneration of sodium aluminum hydride for continuing use of alane as a source of hydrogen.

There is sufficient hydrogen formed to both power the automobile and react with the sodium cation. Zidan says, “Stored hydrogen is typically released during the breakdown of alane at a temperature between 100 C and 150 C. The temperature can be lowered by controlling the particle size of the alane powder. The temperature required for the release process should not drop below 100 C because hydrogen can leak out of the alane.”

One step that proved to be difficult was the isolation of alane from the THF adduct. Zidan says, “We added trieth-

ylamine to the process, which facilitated the formation of an adduct with alane. Free alane was then isolated by heating the adduct under vacuum conditions.”

This research demonstrates the feasibility of using alane in a reversible process to generate a stable hydrogen derivative suitable as a storage material that can readily release the fuel at the right time. In addition, recycling can be done to regenerate the hydrogen-storage material using a process that is efficient and does not involve dealing with thermodynamically unfavorable byproducts.

Zidan believes this process can be used in other applications such as batteries and semiconductors. Additional information can be found in a recent article<sup>2</sup> or by contacting Zidan at [ragaiy.zidan@srnl.doe.gov](mailto:ragaiy.zidan@srnl.doe.gov).

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