Ceria-Supported Platinum as Hydrogen-Oxygen Recombinant Catalyst for Sealed Lead-Acid Batteries

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The lead-acid battery is the most widely used secondary battery in the world. Although conventional lead-acid batteries are considered a mature technology, significant research and development efforts are currently under way to enhance their performance. Since its invention in 1859 by Gaston Planté, many improvements have been made in lead-acid battery technology, and although the essential electrochemistry remains unchanged, modern lead-acid batteries have been claimed to function at about 98% recombination efficiency, with less than 5% loss in their water content over their life span. However, some sealed lead-acid batteries have been reported to fail within 5 years. The use of a hydrogen-oxygen recombinant catalyst, such as the one reported here, will not only improve the performance of sealed lead-acid batteries but would also simplify their process of manufacture and battery cost. This is because the elimination of water loss will lessen the complexities associated with design of acid-limited sealed lead-acid batteries and would thereby provide the possibility of increasing the energy density of the batteries. This would also help to reduce the positive-grid corrosion, which would enhance battery life. A superior hydrogen-oxygen recombination will provide increased uniformity in the float-life characteristics of the battery, and the possibility of using any type of grid which will make the batteries cost-effective. In addition, it would be possible to charge the batteries at faster rates particularly with constant current recharge.

In this paper, we report on a novel ceria-supported platinum catalyst prepared by a rapid solution-combustion reaction and its effectiveness in realizing a sealed lead-acid battery with nearly 100% recombination of hydrogen and oxygen gases, generated during its recharge, into water. As a consequence, there is no net change in the quantity or concentration of the sulfuric-acid electrolyte over the charge-discharge cycles of the lead-acid battery. In addition, because there is almost no rise in the internal pressure of the battery during its operation, it could, in principle, be sealed without any regulatory valve. Thus, the emission of acid fumes which causes corrosion of metallic parts in the vicinity of the battery is completely averted.

Experimental

CeO₂-supported platinum catalyst (2 atom % Pt/CeO₂) employed in the present study was prepared by a rapid solution-combustion reaction. The combustion mixture comprised ceric ammonium nitrate [(NH₄)₂Ce(NO₃)₆], chloroplatinic acid (H₂PtCl₆), and oxalyldihydrazide (C₂H₂N₄O₂) in the molar ratios 0.98:0.02:2.35. Oxalyldihydrazide derived from diethyl oxalate, and hydrazine hydrate acts as the fuel. Initially, 10 g of ceric ammonium nitrate (E-Merck India, 99.9% purity), 0.193 g of chloroplatinic acid (Ranbaxy Laboratories India, 99% purity), and 5.175 g of oxalyldihydrazide were dissolved in a minimum volume of water in a borosilicate-glass dish. Subsequently, the borosilicate-glass dish containing the redox mixture and an appropriate quantity of hydrazine hydrate was introduced into a muffle furnace maintained at 350°C. The solution was found to froth and foam with concomitant loss of water. When the removal of water was complete, the redox mixture ignited with the flame temperature at ca. 1000°C yielding a voluminous and finely dispersed ceria-supported platinum catalyst as a solid product within about 5 min.

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A powder X-ray diffraction (XRD) pattern of the 2 atom % Pt/CeO₂ catalyst thus prepared was obtained on a Siemens D-5005 X-ray diffractometer using CuKα-radiation at a scan rate of 2° min⁻¹. The Brunauer-Emmett-Teller (BET) surface area of the catalyst was measured on a Carlo-Erba Sorptomatic-1900 surface-area analyzer. Electron micrographs of the catalyst were obtained on a JEOL JEM-200CX transmission electron microscope (TEM). The X-ray photoelectron spectrum (XPS) of the catalyst was recorded on an ESCA-3 Mark-II VGScientific spectrometer using AlKα-radiation.

Lead-acid batteries (6 V, 3.5 Ah) were constructed from fully formed negative-lead and positive-lead oxide plates using aq. H₂SO₄ (sp.gr. = 1.25) in a Plexiglas container with three compartments to house the constituent lead-acid cells connected in series. The batteries were sealed with each of the cells having a plug containing 100% conversion for H₂ + 1/2 O₂ → H₂O reaction.

Figure 1. XRD patterns of the 2 atom % Pt/CeO₂ catalyst (A) as prepared and (B) after soaking in strong sulfuric acid for a prolonged duration.

Results and Discussion

Powder XRD pattern for the as-prepared 2 atom % Pt/CeO₂ catalyst is shown in Fig. 1A. The XRD pattern agrees well with CeO₂ in fluorite structure. The XRD pattern was devoid of any diffraction lines due to Pt-metal particles or any oxides of platinum. To establish the stability of the catalyst in concentrated sulfuric acid and strong aq. KOH, we soaked the catalyst in these mediums for prolonged periods and subsequently recorded their XRD patterns as shown in Fig. 1B. There is little difference in XRD patterns suggesting the stability of the catalyst both in sulfuric acid and aq. KOH. The catalyst has a surface area of ~18 m² g⁻¹, TEMs of the catalyst depict the absence of any platinum particles on ceria support.

In Fig. 2, we show the Pt (4f) X-ray photoelectron spectrum of the 2 atom % Pt/CeO₂ catalyst. The spectrum could be deconvoluted into only two components labeled as 1 and 2 at respective binding energies of 71.9 and 74.4 eV. We can assign the 4f7/2 signal at 71.9 eV to Pt²⁺ and the signal at 74.4 eV to Pt⁴⁺ species. Interestingly, the spectrum showed complete absence of metallic or zero-valent platinum species in the catalyst since the signal associated Pt-4f7/2 at 71.1 eV for Pt metal is altogether absent. These data suggest that platinum in the catalyst is present only in Pt²⁺ and Pt⁴⁺ states. As would be discussed later, Pt²⁺ and Pt⁴⁺ species facilitate the H₂ + 1/2 O₂ → H₂O reaction.

After finding the ceria-supported platinum catalyst to exhibit 100% conversion for H₂ + 1/2 O₂ → H₂O reaction (~100 μmol g⁻¹ s⁻¹) at room temperature, attempts were made to test it as hydrogen and oxygen recombinant catalyst in lead-acid batteries. For this purpose, lead-acid batteries were assembled, both with and without the ceria-supported catalyst plugs, with the provision to measure the buildup of gaseous pressure in the battery. Typical galvanostatic charge-discharge data for such a lead-acid battery at 25°C and at C/5 rate are shown in Fig. 3. The data suggest a faradic efficiency of about 90%. In Fig. 4A and B, we show the variation in the internal pressure of the battery and catalyst-bed temperature as the function of battery charging rates at 25°C, respectively. From the data in Fig. 4A, it appears that the pressure of the gases evolved while charging the battery rises initially but then decreases and stays between 1-4 kN m⁻² depending on the rate of battery charging. Similarly, the data in Fig. 4B suggest that the catalyst-bed temperature increases when evolution of gases starts, owing to the exothermicity of the hydrogen-oxygen recombination reaction, but finally remains invariant between 50-60°C depending on the charging rate of the battery. To examine the performance of the catalyst at lower temperatures, we also conducted these experiments at C/5 rate of battery charging at ~5 and 10°C, and the data are shown in Fig. 5. Here too, the gaseous pressure initially rises but finally stabilizes between 0.5-0.7 kN m⁻² depending on the battery charging rate. In a similar fashion, the catalyst-bed temperature initially rises as the recombination of gaseous hydrogen and oxygen begins but thereafter stays between 50-60°C.

Figure 2. Pt (4f) XPS of the 2 atom % Pt/CeO₂ catalyst.
23-25°C. We did not observe any freezing in the catalyst as reported in the literature for other recombinant catalysts. By contrast, the batteries without the catalyst plug showed a continuous rise in the gaseous pressure. Similar experiments were carried out with commercial grade 2 V 200 Ah VRLA cells at 30°C at various charging rates between C and C/10. While there was a continuous increase in the gaseous pressure beyond 2.6 V with cells without the catalyst plug, no increase in gaseous pressure was observed with cells fitted with the catalyst plug. These data suggest a complete recombination of hydrogen and oxygen gases evolved during the charging of the VRLA cells fitted with the catalyst plug. On the basis of XPS data (Fig. 2), we suggest that the recombination of hydrogen and oxygen into water on the catalyst occurs through the mechanism shown in Fig. 6.

The battery with the recombinant-catalyst plug has been subjected to over 100 charge-discharge cycles with almost no change in the electrolyte level or battery capacity. During prolonged operation of the battery, we observed little variation in its internal resistance, which usually arises due to a change in the specific gravity of the sulfuric-acid electrolyte. This would enhance the life span of the battery substantially. We consider it a major step forward in lead-acid battery technology. The catalyst is equally effective for recombining hydrogen and oxygen in sealed alkaline-storage-batteries. The catalyst will be particularly advantageous in realizing commercially viable sealed nickel-iron batteries. In the past, nickel-iron batteries have been shown to sustain both mechanical and electrical abuse, and have been found to provide cycle life of over 3000 charge-discharge cycles with a calendar life of about 20 years. But nickel-iron batteries have failed to make any commercial impact.

![Figure 3](image1.png)  
**Figure 3.** Typical charge-discharge data for a sealed lead-acid battery assembled for the present study.

![Figure 4](image2.png)  
**Figure 4.** (A) Internal gas-pressure and (B) catalyst-bed temperature observed while charging a sealed lead-acid battery having the recombinant catalyst-plug at C/2, C/5, and C/10 rates at 25°C.

![Figure 5](image3.png)  
**Figure 5.** (A) Internal gas-pressure and (B) catalyst-bed temperature observed while charging a sealed lead-acid battery having the recombinant catalyst-plug at C/5 rate at -5 and 10°C.

![Figure 6](image4.png)  
**Figure 6.** Mechanism of hydrogen and oxygen recombination to water on Pt/CeO$_2$ catalyst.
primarily because it has not been possible to seal these batteries owing to the insurmountable difficulty of recombining hydrogen and oxygen gases.39

In summary, the solution-combustion method employed here yields ionically substituted platinum sites on nanosized ceria crystallites which has 100% efficiency for H2 + 1/2O2 → H2O reaction and hence can be effectively used as a hydrogen-oxygen recombinant catalyst in sealed lead-acid batteries. This will help in maintaining the batteries with little change in their internal resistance and float currents during their service life. In addition, with the use of recombinant catalyst, it would be possible to eliminate premature battery failures arising due to the negative-plate sulfating and positive-grid corrosion. Furthermore, the use of the recombinant catalyst will make the batteries more design-flexible to grid-alloy compositions, and free from positive-plate capacity limitations as well as void-volume requirements of the battery separator. We strongly believe that it would be possible to realize a safer and totally sealed lead-acid battery with the use of this recombinant catalyst.

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