



# Enhancement of NO<sub>x</sub> removal performance for (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.99</sub>MnO<sub>3</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> electrochemical cells by NO<sub>x</sub> storage/reduction adsorption layers

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## ABSTRACT

This study investigated the effect of adding a NO<sub>x</sub> adsorption layer to the cathode of an electrochemical cell on the removal of NO<sub>x</sub> from gaseous mixtures. The cathode was a composite of (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.99</sub>MnO<sub>3</sub> (LSM15) and Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (CGO10). Two different kinds of adsorption layers, K–Pt–Al<sub>2</sub>O<sub>3</sub> layer and Ba–Pt–Al<sub>2</sub>O<sub>3</sub> layer (known as NO<sub>x</sub> storage/reduction (NSR) catalyst), were studied. The effects of the NSR adsorption layers on the electrode processes were characterized by electrochemical impedance spectroscopy (EIS). Both adsorption layers increased the reduction of NO<sub>x</sub> to N<sub>2</sub> in an atmosphere that contained only NO. When O<sub>2</sub> was present with NO in the atmosphere, the K–Pt–Al<sub>2</sub>O<sub>3</sub> adsorption layer significantly enhanced the conversion of NO<sub>x</sub> to N<sub>2</sub>, but the Ba–Pt–Al<sub>2</sub>O<sub>3</sub> adsorption layer had no effect. The selective removal of NO<sub>x</sub> under O<sub>2</sub>-rich conditions was achieved by modifying the LSM15/CGO10 cell with a suitable NSR adsorption layer. The improvement for NO<sub>x</sub> reduction by the adsorption layers was mainly contributed by the promotion of the adsorption and surface diffusion of NO<sub>x</sub> species at/near the triple phase boundary (TPB) regions of the electrode and probably the formation of a short and effective reaction path for NO<sub>x</sub> reduction. A stronger capability for oxidizing NO and/or trapping NO<sub>x</sub> under the test conditions may have contributed to the superior performance of the K–Pt–Al<sub>2</sub>O<sub>3</sub> adsorption layer relative to the Ba–Pt–Al<sub>2</sub>O<sub>3</sub> layer.

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## 1. Introduction

The use of diesel engines is becoming more widespread because their fuel economy is superior to and their emission levels of carbon monoxide and carbon dioxide are considerably lower than those of gasoline engines. However, the high-temperature combustion in diesel engines generates significant amounts of nitrogen oxides (NO<sub>x</sub>) [1], which have harmful effects on the environment [3–5] and human beings [6], and are limited by increasingly stringent government regulations worldwide [7]. Traditional three-way catalysts are incapable of reducing NO<sub>x</sub> in O<sub>2</sub>-rich diesel engine exhaust [2]. Therefore, there is a great demand for new technology to control NO<sub>x</sub> emissions in diesel engine exhaust. Research efforts currently focus on two approaches [8]. The first approach uses selective catalytic reduction (SCR) catalysts to selectively reduce NO<sub>x</sub> but requires additional reducing agents (ammonia, urea, and

so forth), which introduce problems related to storage, spill management, and development of a distribution network. The second approach, represented by NO<sub>x</sub> storage/reduction (NSR) catalysts, achieves NO<sub>x</sub> reduction by selectively storing NO<sub>x</sub> under lean conditions, and subsequently reducing the stored NO<sub>x</sub> under rich switch. However, a sophisticated, adaptive control system is needed to implement this approach in mobile applications.

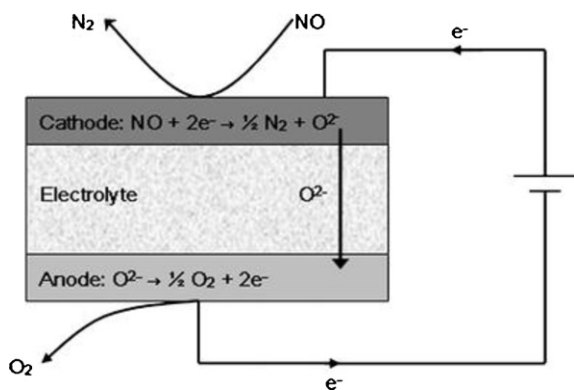
An alternate approach is to reduce NO<sub>x</sub> to N<sub>2</sub> on the polarized cathode in a solid state electrochemical cell, Fig. 1 [9]. This technology was first introduced by Pancharatnam et al. [10] in 1975 for a zirconia-based cell under O<sub>2</sub>-free conditions. Cicero [11] and Hibino et al. [12–14] subsequently demonstrated that this approach can also work in the presence of O<sub>2</sub>. Since then, different studies [15–21] have identified suitable cathode materials or optimized the cell structure to improve its NO<sub>x</sub> removal properties. With this approach, the inherent challenge is to selectively reduce NO<sub>x</sub> (rather than O<sub>2</sub>) in an O<sub>2</sub>-rich environment without consuming large amounts of electrical power.

In this study, (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.99</sub>MnO<sub>3</sub> (LSM15)/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (CGO10) cathodes are coated with NO<sub>x</sub> adsorption layers made of NSR catalysts. The NO<sub>x</sub> removal performance of blank cells (with uncoated cathodes) and cells with cathodes coated with two different kinds of NSR adsorption layers are tested and compared.

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**Fig. 1.** Illustration of  $\text{NO}_x$  reduction on a solid state electrochemical cell (reprinted with permission from Ref. [9]; copyright 2012 Springer).

The underlying motivation of this study is to solve the selectivity challenge of electrochemical cells by combining it with NSR catalyst and using electrical polarization instead of rich conditions to reduce stored  $\text{NO}_x$  on an NSR catalyst. With this approach, the engine is operated continuously under lean conditions (to avoid the fuel penalty), and a complicated control system is no longer needed. Furthermore, no additional reducing agents are needed other than electrons. Previous work by Hamamoto et al. [22,23] and our group [24] showed that NSR adsorption layers improved the performance of electrochemical cells. However, the cathode materials in the current work involve the use of noble metals (Pt, Pd) and a reactive material (Ni). The continuous redox reaction between Ni and NiO during cell operation causes volume expansion that would eventually deteriorate the cell structure [25]. In this work, LSM15 and CGO10 were chosen as the cathode materials. LSM15 has good stability and is widely used as a material for cathodes in solid state fuel cells (SOFC) [26]. The ionic conductivity of CGO10 at low temperatures ( $<600^\circ\text{C}$ ) is superior to that of YSZ [27]. In addition to performance measurements, detailed characterizations by electrochemical impedance spectroscopy (EIS) were also performed to identify the effects of adsorption layers on electrode processes for the electrochemical reduction of  $\text{NO}_x$ .

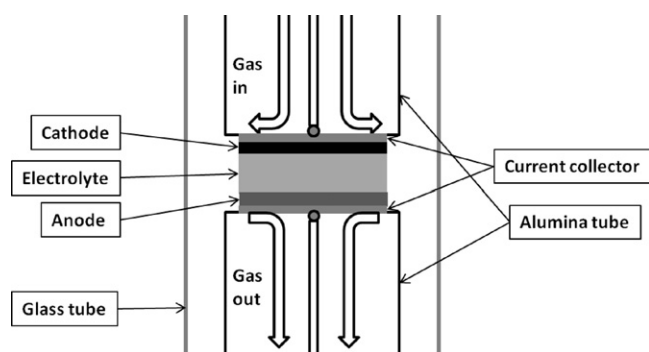
## 2. Experimental

### 2.1. Cell fabrication

Three kinds of cells were prepared and tested in this study:

- (1) Blank cells.
- (2) Cells with K–Pt– $\text{Al}_2\text{O}_3$  adsorption layers.
- (3) Cells with Ba–Pt– $\text{Al}_2\text{O}_3$  adsorption layers.

The last two types of cells were prepared by coating an adsorption layer on the cathode side of the blank cell. The blank cell was supported on a  $200\ \mu\text{m}$  thick CGO10 tape (Kerafol, Germany). The cathodes were prepared by screen printing a composite slurry on one side of the tape and sintering at  $1150^\circ\text{C}$  for 2 h. The slurries contained equal amount of LSM15 (Haldor Topsøe, Denmark) and CGO10 (Rhodia, France) powders. The anodes were prepared by painting Pt paste (Ferro) on the other side of the tape and sintering at  $900^\circ\text{C}$  for 1 h. The active area of the cathode was  $1.54\ \text{cm}^2$ , the same as that of the anode. The thicknesses of the cathode and anode layers were both approximately  $10\ \mu\text{m}$ . A mesh-patterned Au layer was painted over the cathode, sintered at  $700^\circ\text{C}$  for 1 h, and used to collect the current. An Au wire was connected to the Au layer when the cell was coated with an adsorption layer.



**Fig. 2.** Sketch of the test setup for electrochemical cells.

The adsorption layer was applied by dripping several drops of adsorbent solution on top of the cathode, drying at  $110^\circ\text{C}$  for 12 h, and heating at  $550^\circ\text{C}$  for 1 h. The amount of the adsorption layer coated on the cathode was approximately  $8\ \text{mg cm}^{-2}$  with a thickness of approximately  $50\ \mu\text{m}$ . The adsorbent solution was prepared by dispersing the adsorbents in distilled water with some surfactants. The adsorbents consisted of 10 wt% K with 3 wt% Pt supported on  $\text{Al}_2\text{O}_3$  nanopowders for the K–Pt– $\text{Al}_2\text{O}_3$  system, and 20 wt% Ba with 1 wt% Pt for the Ba–Pt– $\text{Al}_2\text{O}_3$  system. These two compositions were chosen because they are commonly used as NSR catalysts. The adsorbents were prepared from  $\text{Al}_2\text{O}_3$  powders (Alfa Aesar, Germany, metal basis) that were dissolved in distilled water with vigorous stirring. The  $\text{Al}_2\text{O}_3$  suspensions were mixed with a solution of  $\text{KNO}_3$  (Alfa Aesar, Germany, 99%) or  $\text{Ba}(\text{NO}_3)_2$  (E. Merck Dam., Germany, 99+%) and a solution of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  (Aldrich, Germany, 99.995%). Each mixture was stirred and heated until a thick paste remained. Each paste was stored at  $120^\circ\text{C}$  overnight and then at  $200^\circ\text{C}$  for 2 h to completely dry the powder. Then, the powders were milled and sintered at  $600^\circ\text{C}$  for 1 h.

### 2.2. Performance measurement of $\text{NO}_x$ removal

The three kinds of cells were examined under the same conditions. The cells were installed in a glass tube apparatus (Fig. 2). Two pieces of Au mesh were placed on both sides of each cell as current collectors. The apparatus was placed inside a furnace and connected to a Gamry Reference 600 potentiostat. Before the conversion measurements, all the samples were pretreated in 1000 ppm NO with 8%  $\text{O}_2$  in Ar at  $350^\circ\text{C}$  for 2 to 4 h in order to remove the carbonates and hydroxides of potassium or barium that potentially co-existed in the adsorption layers with the oxide. The cells were polarized from  $-1$  to  $-2.5\ \text{V}$  for 10–15 min in the temperature range between  $300$  and  $500^\circ\text{C}$ . The gases used to test the cells consisted of 1000 ppm NO and 1000 ppm NO with 8%  $\text{O}_2$  in Ar with a flow rate of  $2\ \text{L/h}$  that was maintained by Brooks mass flow controllers. The outlet gas composition was monitored throughout the test by chemiluminescence (Model 42i HL, Thermo Scientific, USA) for NO,  $\text{NO}_2$  and  $\text{NO}_x$  and mass spectrometry (Omnistar GSD 301, Pfeiffer Vacuum, Germany) for  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_2$ . A small leak ( $250$ – $300\ \text{ppm N}_2$  and  $70$ – $100\ \text{ppm O}_2$ ) in the gas lines was detected by mass spectrometry. Two replicates of each kind of cell were tested and gave results with good reproducibility.

### 2.3. Impedance characterization of electrode performance

Impedance spectra were recorded with a Gamry Reference 600 potentiostat over a frequency range from  $1 \times 10^6$  to  $0.001\ \text{Hz}$  with 6 data points per decade and  $36\ \text{mV rms}$  amplitude. To study the characteristics of the impedance spectra, a series of variations in the experimental conditions were made, including temperature,

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