Chemical Traps

An Electrochemically Driven and Electrochemically Regenerated NO_x Trap[**]

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Absorption traps are used in a wide variety of different applications to prevent potentially harmful chemicals from entering the environment and/or from coming into contact with sensitive downstream equipment. Many of the materials in use cannot be regenerated so that concerns relating to sustainable usage and environmentally acceptable disposal are important; in other cases, regeneration can only be accomplished with relative difficulty. Herein we describe a new principle that can be used to address both these issues.

A key application where chemical traps have found widespread use is in the control of NO_x emissions generated by fuel-efficient automotive engines which, by reducing the atmospheric CO_2 burden, can significantly mitigate the impact of road transport on global warming. Unfortunately, such engines produce much higher concentrations of nitrogen oxides (NO_x) than conventional gasoline engines[1] with attendant adverse impact on human health and the environment.[2] As a consequence, conventional "three-way" catalytic converters are inadequate and a post-converter NO_x trap is required. These traps consist of an alkaline-earth component (usually barium) that is able to store NO_x species as various nitrates and nitrites under the oxygen-rich conditions typical of "lean" engine operation. Precious metals, usually platinum, are also used as they aid in the uptake of NO_x by providing sites for the adsorption and catalytic oxidation of NO to NO_2. To restore the trap the engine is momentarily switched to "rich operation", generating a large concentration of reducing species that cause reduction of the adsorbed nitrate/nitrite species to nitrogen thus regenerating the active $BaO/BaCO_3$ component. A disadvantage of this procedure is that relatively high temperatures (≈ 900 K) are required for complete regeneration. Although the current generation of NO_x traps is very effective when run under these conditions, a number of significant problems remain, especially the need for regular high-temperature excursions, the requirement of periodic rich engine operation (which partially defeats the object of lean operation), and susceptibility to poisoning by sulfur compounds present in the fuel.

Herein we report a novel electrochemically driven NO_x trap that can operate effectively over a range of temperatures and can be regenerated as required in a controlled manner, without the requirement for temperature excursions or changes in gas-phase composition. Although NO_x trapping is used herein to illustrate the technique, the general method employed could be applicable in a wide variety of different applications, including, for example, removal oxides of carbon and sulfur. The trap consists of a thin porous layer of a precious metal (Pt, Pd, or Rh) deposited onto the surface of a solid electrolyte wafer that is biased to deliver the active species to the metal surface where it encounters the adsorbed NO_x. We used sodium and potassium ionic conductors although a variety of other solid electrolytes could be used, depending on the application.

NO_x-trapping and trap-regeneration measurements were performed in a well-mixed microreactor operated at atmospheric pressure and described in detail elsewhere.[3] X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG ADES 400 spectrometer system[4] and in situ infrared spectroscopy measurements were performed with a Perkin Elmer GX2000 spectrometer utilizing a Harrick Refractor Reactor specular reflection accessory.

The performance of the trap is illustrated in Figure 1 which shows the effects of 1) electrochemically trapping NO_x

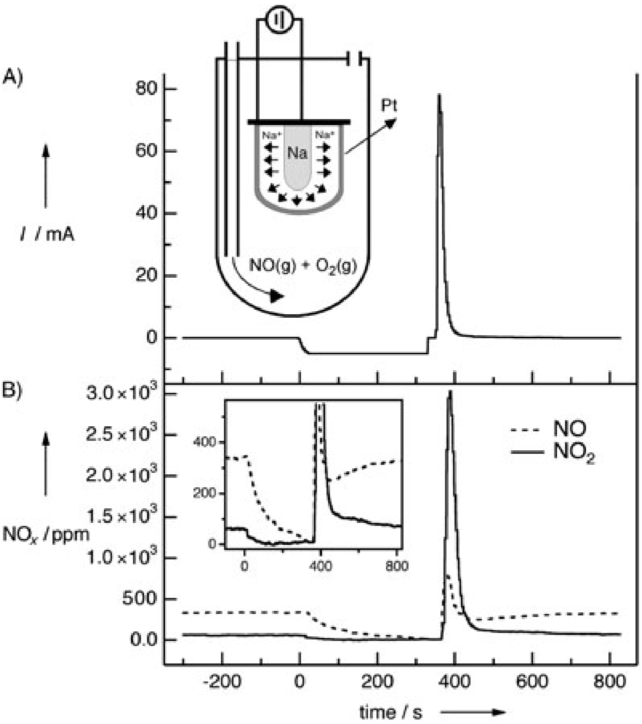

Figure 1. Trapping and regeneration carried out with a Pt|Na–β″alumina|Na electrochemical cell as shown in the inset of (A). A) Variations in the galvanic current passed through the trap and B) the composition of the exit gas. The counter electrode (metallic sodium) is not in contact with the gas atmosphere. Gas feed was 400 ppm NO_x + 5% O_2 at 150 mL min^{-1} at 573 K. Initial reactant feed at open circuit, negative current imposed at $t=0$ (A) resulting in electrochemical pumping of sodium towards the Pt electrode and NO_x trapping from the gas phase (B). Inset in (B) shows gas-phase composition over 0–800 s interval in more detail. Reversing the current decomposes the trapped nitroxy species resulting in the desorption of mainly NO_2.

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and subsequent 2) trap regeneration with release of (mainly) NO_2. Initially, under open circuit conditions with trap at 573 K, the exit gas composition (identical to the inlet gas composition) was 340 ppm NO, 60 ppm NO_2 and 5 % O_2. These concentrations are representative of lean-burn engine exhaust. At $t=0$ a constant current of -5 mA (4.2×10^{-4} A cm^{-2}, ca. 10 V) was applied between the counter and working electrodes, by means of a galvanostat, driving sodium ions to the surface of the porous platinum film where they were discharged at the three-phase boundary ($Na^+ + e^- \rightarrow Na$) the sodium then reacted with ambient gas, trapping NO_x. Within approximately 10 s of current application the exit concentration of NO_x from the reactor declined reaching a value of 15 ppm after 300 s of current flow which corresponds to 95.5 % removal of NO_x and essentially 100 % suppression of NO_2. (Note that in our experiment the apparent time dependence of NO_x uptake is entirely determined by the mean residence time of gas molecules in the trap (ca. 60 s) and not by the intrinsic rate of trapping). The trap was then switched to open circuit for 15 s after which it was polarized in the opposite sense. This resulted in a current spike of approximately +80 mA (6.7×10^{-3} A cm^{-2}) which correlated with a very large release of NO_x which consisted principally of NO_2 accompanied by a small quantity of NO. This feature is important because NO_2 is much more reactive than NO towards the reductant species present in engine exhaust (CO, H_2, hydrocarbons).[5] Its production during trap regeneration is therefore an additional advantage because it implies much more efficient conversion of stored NO_x into N_2, hence cleaner operation, under practical conditions. Integration of the current/time curves in Figure 1 showed that the amounts of sodium pumped to/from the trap during the trapping/regeneration cycle were equal—that is, there is no loss of Na during operation. The nitrogen balance obtained by integrating the NO_x curves (N trapped during NO_x uptake versus N desorbed during regeneration) closed within 4 %. This behavior was reproducible and repeated in a number of separate experiments.

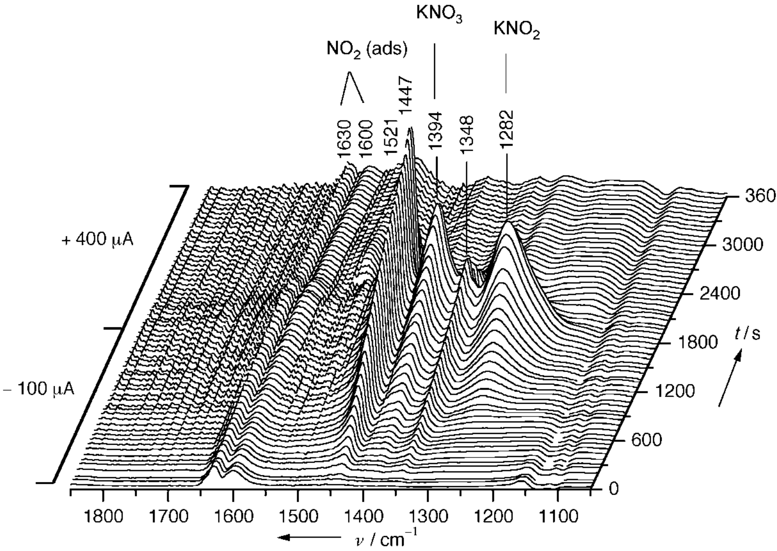

Figure 2. In situ reflectance infrared spectroscopy measurements determine the nature of the nitroxy species resulting from NO_x trapping. Experiments were performed using a Pd | K–β″alumina | Au cell with 400 ppm NO_x + 5 % O_2, 150 mL min^{-1}, at 423 K. A negative current traps NO_x; a positive current decomposes the surface compounds, restoring the initial condition.

To investigate the nature of the species generated by NO_x uptake a separate set of experiments was performed under very similar conditions using an in situ reflectance infrared spectroscopy cell. The data presented in Figure 2 were obtained with a palladium metal film deposited onto a K–β″Al_2O_3 electrolyte wafer, spectra were recorded every 60 s with currents of -100 μA and +400 μA being used to drive K^+ ions to and from the metal surface, respectively. Prior to current application (spectrum at $t=0$ in Figure 2), bands were observed at 1630 and 1600 cm^{-1}, which are characteristic of adsorbed NO_2 on palladium sites.[6] Following current application, two bands developed ($t=180$ s) at 1447 cm^{-1} and 1348 cm^{-1}. The ratio of their intensities was constant indicating that they were due to the same chemical species. On the basis of the observed frequencies these bands are assigned to the symmetric and asymmetric stretches of a highly dispersed potassium nitrite species.[6] Subsequently, a band appeared at 1394 cm^{-1} which may be confidently assigned to bulk-like KNO_3,[6] indicating the onset of three-dimensional growth of nitrate crystallites on the palladium surface. Finally, ($t=900$ s) a band appeared at 1282 cm^{-1} which may be assigned to bulk-like KNO_2.[6]

After 1800 s the current direction was reversed ($I=400$ μA), thus pumping potassium ions away from the surface. This change resulted in a rapid decline in the intensity of all the bands between 1200 and 1500 cm^{-1}, directly demonstrating the electrochemically induced decomposition of the various nitrate/nitrite species. Clearly, the evolution of surface species with amount of charge passed is in very good accord with variations in gas composition at the trap exit. (The small remaining feature at 1521 cm^{-1} is assigned to residual nitrate on the palladium surface.)

Further confirmation of the electrochemically induced formation and destruction of NO_x-storing surface species and of their chemical identity was obtained by ex situ XPS (Figure 3). The pumping of Na to and from the Pt surface and the concomitant accumulation and destruction, respectively, of alkali metal nitrate and nitrite are clearly apparent.[7] Thus the XPS findings are in complete agreement with the trapping/regeneration behavior and the in situ IR results. Note that the spectroscopic measurements called for compact samples and as a result truly reversible alkali metal counter electrodes were impractical. Although irreversible in the strict sense, the Au electrodes employed behaved reversibly over many cycles because in any given experiment the extent of alkali depletion of the bulk electrolyte was negligible and was restored when the current was reversed.

Optimization of trap design, for example to improve gas throughput and active trapping surface area, are important practical issues that remain to be addressed—however these are beyond the aim of this report. Our object was to demonstrate a novel concept: a solid-state electrochemical device that operates at modest temperatures, stores NO_x very

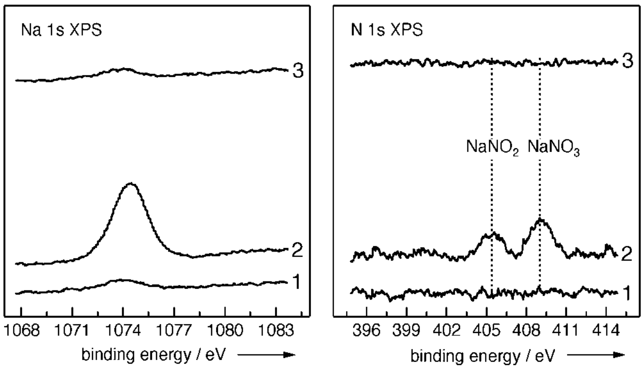

Figure 3. Na 1s (left) and N 1s (right) XP spectra obtained using a Pt|Na–β″alumina|Au cell after exposing the Pt electrode to a reactive gas atmosphere (0.1% NO + 5% O_2 at 473 K) under open circuit conditions (spectra 1), after pumping Na to the Pt electrode (spectra 2), and after pumping Na away from the Pt electrode (spectra 3).

effectively, and can be efficiently regenerated isothermally. In terms of practical application, the stability of an electrochemical trap device against long-term degradation by water vapor in the gas stream represents a materials issue that would have to be solved. In this regard K–β″aluminas are significantly more stable in the presence of water vapor than Na–β″aluminas. For example, they survive long periods at 900 K/15% humidity/atmospheric-pressure conditions that are more severe than those that would be encountered in the application envisaged here.[8] Moreover, NASICON-type alkali metal ion conducting ceramics, an alternative class of materials that could be used, exhibit transport properties that are independent of water vapor pressure and can have good stability in wet atmospheres.[9]

Conventional NO_x traps have a storage capacity of approximately 1 gNO/litre of trap volume before regeneration is necessary. Our trap had an effective volume of 3×10^{-3} litre and the data presented in Figure 1 correspond to storage of 0.13 gNO/litre of trap volume over the course of this experiment. A $NaNO_3$ film of 60 nm thickness (readily attainable with our system) equates to a maximum theoretical trapping capacity of 1 gNO/litre so that the achievable trapping capacity should be at least as good as that with conventional traps.

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