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Published in:
Journal of The Electrochemical Society

Link to article, DOI:
[10.1149/1.1566413](https://doi.org/10.1149/1.1566413)

Publication date:
2003

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Petrushina, I., Bandur, V., Cappeln, F. V., Bjerrum, N., Sørensen, R. Z., Refshauge, R. H., & Li, Q. (2003). Electrochemical promotion of NO reduction by hydrogen on a platinum/polybenzimidazole catalyst. *Journal of The Electrochemical Society*, 150(5), D87-D90. <https://doi.org/10.1149/1.1566413>

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Electrochemical Promotion of NO Reduction by Hydrogen on a Platinum/Polybenzimidazole Catalyst

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The electrochemical promotion of catalytic NO reduction by hydrogen was studied using a (NO, H₂, Ar), Pt polybenzimidazole (PBI)-H₃PO₄|Pt, (H₂, Ar) fuel cell at 135°C. A mixture of NO/H₂/Ar was used as the working mixture at one electrode and a mixture of H₂/Ar was used as reference and counter gas at the other electrode. Products of NO reduction (N₂ and H₂O) were analyzed by an on-line mass spectrometer. At high NO + H₂ + Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure) the maximum rate enhancement ratio was 4.65. At low NO + H₂ + Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively), NO reduction increased 20 times even without polarization compared to the high gas flow rate. The electrochemical promotion effect occurs at positive polarization with a maximum increase at approximately 0.08 V and with 1.5 times the zero polarization value. The promotion at the negative polarization can be attributed to the electrochemical production of the promoters. At low gas flow rates, a charge-induced change of the strength of chemisorptive bonds can take place.
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Manuscript submitted August 27, 2002; revised manuscript received December 5, 2002. Available electronically March 28, 2003.

The present work is a continuation of our research in the fields of electrochemical promotion¹ and polymer electrolyte fuel cells.^{2,3} That a catalyst is often a system which consists of an electronic and an ionic conductor makes it possible to use electrochemical techniques to study the nature of the promotion effect in catalysts. Application of galvanic cells with solid electrolytes for the study of catalytic phenomena was suggested by Wagner.⁴ Later, Vayenas *et al.*⁵ found that rate and selectivity of a catalytic reaction can be remarkably and reversibly changed by electrochemical polarization of the electronic conductive catalyst on an ionic conductive support. This phenomenon was named NEMCA effect (nonfaradaic electrochemical modification of catalytic activity) or electrochemical promotion.⁴ The NEMCA effect has been demonstrated for more than 50 heterogeneous^{2,5-22} and one homogeneous¹ catalytic reactions. According to Vayenas *et al.*,⁵⁻¹⁰ the NEMCA effect can be described by the following parameters. The rate enhancement ratio

$$\rho = r/r_o \quad [1]$$

and the enhancement factor

$$\Lambda = (r - r_o)/(1/2F) \quad [2]$$

where r is the catalytic rate at current I , r_o is the open-circuit catalytic rate, and F is Faraday's constant. In all studied cases of the electrochemical promotion $|\Lambda| \gg 1$ and that was the reason for this effect being called nonfaradaic.

Vayenas *et al.*⁵⁻¹⁰ explained the electrochemical promotion of a catalyst as an effect of changes in the work function, $e\Delta\Phi$ (e is the electron charge, $\Delta\Phi$ is change of the electron extraction potential), of the catalyst under polarization. The change of the electron extraction potential has been measured to be equal to the applied polarization, *i.e.*

$$\eta = \Delta\Phi \quad [3]$$

It was also suggested that this change in the work function was caused by spillover of the products of the charge transfer from the three-phase boundary to the catalyst-gas interface. The change in the work function was measured using the Kelvin probe technique.

However, it has been found later¹⁸⁻²² that work function changes of catalyst with different morphology, measured using a Kelvin

probe, may be only a part of the applied polarization or do not change at all. Summarizing the results of Refs. 5-22, one can agree with the assumption of Emery *et al.*²⁰ and Metcalfe^{21,22} that

$$\Delta\Phi = \xi\eta \quad [4]$$

where ξ is a coefficient. Furthermore one can also assume $0 \leq \xi \leq 1$.

The electrochemical potential of the electron in a metal, $\bar{\mu}_e$ (Fermi level), is a sum of the chemical potential of the electron in the metal μ_e and $e\phi$, where ϕ is the inner or Galvani potential. The Galvani potential is a sum of an outer (or Volta) potential, Ψ , and a surface potential, χ . The work function of electron, $e\Delta\Phi$, is equal to the electrochemical potential of the uncharged metal ($\Psi = 0$),²³ *i.e.*

$$\Delta\Phi = \Delta\mu + \Delta\chi \quad [5]$$

and $\Delta\Psi \neq 0$ is the reason for the difference between $\Delta\Phi$ and η (Eq. 4). The value of ξ is defined by the value of the polarization resistance of the electrochemical reaction at the catalyst support interface: if this resistance is low, $\xi \approx 1$; if this resistance is high, $\xi \approx 0$ and by polarization we mainly charge the catalyst-support electric double layer.²⁰

In our previous paper² we have defined three types of electrochemical promotion depending on values of the faradaic current (I) and Λ , however it is more precise to separate electrochemical promotion and electrocatalysis.

1. The electrochemical promotion effect is the charge-induced change of the strength of chemisorptive bonds at the catalyst-support-reactant boundary in heterogeneous catalysis or electrode-catalyst interface in homogeneous catalysis (CI effect). The CI effect is characterized by $I = 0$, $\eta = \Delta\Psi$, and $\Delta\Phi = 0$. In this case the catalyst (or an electrode in homogeneous catalysis) is charged to the potential of the specific adsorption of one or more reactants.

2. The electrochemical promotion effect is the effect induced by the electrochemical production of the catalyst promoters (EPP effect). $I \neq 0$; $\Lambda \gg 1$; $\Delta\Psi = 0$, and $\Delta\Phi = \eta$. The electrocatalytic effect is a separate case where the reactant (or reactants) of a catalytic reaction is (are) oxidized or reduced electrochemically, $I \neq 0$, $\Lambda \approx 1$.

Most published cases of electrochemical promotion²⁻¹³ can be ascribed to the EPP effect or mixed CI and EPP effects, depending on the polarization resistance of the EPP reaction. The promotion of the homogeneous catalytic reaction¹ or alkene isomerizations¹⁶ are examples of the CI effect.

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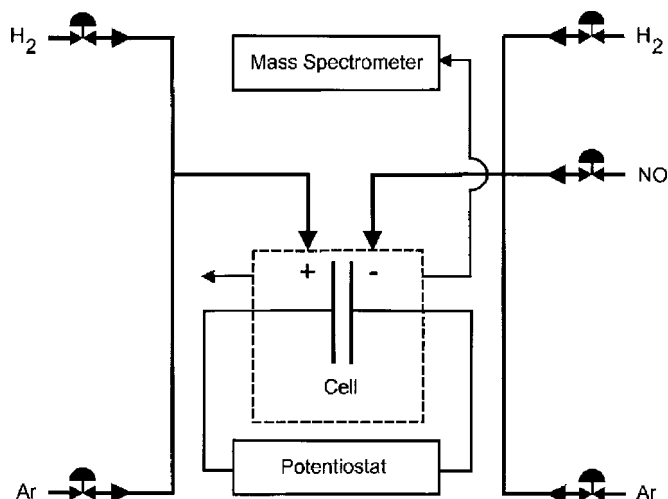


Figure 1. Setup for study of electrochemical promotion of catalytic reduction.

In most previous studies of electrochemical promotion of the catalytic NO reduction, Na was pumped to the surface of the catalyst using electrochemical reduction of Na^+ ions from Na β'' -alumina support.¹¹⁻¹⁴ This supply of Na greatly enhanced the reduction of NO on Pt, Pd, Rh, and several other catalytic materials with a reaction rate enhancement as high as two orders of magnitude. Simultaneously the selectivity of production of N_2 against N_2O increased. Lambert *et al.*¹¹⁻¹⁴ showed that the effect of electrochemical promotion is equivalent to the effect seen from depositing Na chemically on the catalyst surface. It means that the effect had a pure EPP nature.

The reason for NO reduction being promoted so remarkably is that the supply of Na to the catalytic surface changes the electronic properties of the surface. This happens in a way that strengthens the N-catalyst bond at the expense of the N-O bond, thereby facilitating the dissociation of NO, which is the limiting step of the whole reaction.²⁴ As N_2O is produced by $\text{NO} + \text{N}(\text{ads}) \rightarrow \text{N}_2\text{O}$, the fast dissociation of NO diminishes the production of N_2O .²⁴

The electrochemical promotion of NO reduction is increased with the loading of Na until a certain point, where the supply of any more Na leads to a poisoning of the system.¹² This poisoning happens because when too much Na is present, it and O_{ads} from the NO dissociation begin to cover most of the active centers blocking out new NO molecules.

Electrochemical promotion of NO reduction also took place when the catalyst support was an O^{2-} conductor. For this kind of system, an increase in NO reduction rate (up to $\Lambda = 700$) was obtained when O^{2-} was removed from (or in some cases added to) the catalytic surface.^{9,10,15,17}

In the present research the electrochemical promotion of catalytic NO reduction by hydrogen was studied using a



fuel cell.²⁵ Our purpose was to study the possibility of promoting NO reduction with the adsorbed hydrogen atoms produced electrochemically.

Experimental

The setup for study of electrochemical promotion of the catalytic NO reduction is given in Fig. 1. The carbon-supported Pt catalyst with Pt load around 0.5 mg/cm^2 was used in this investigation.³ The electrolyte was PBI doped with H_3PO_4 . The techniques of preparing the PBI(H_3PO_4) membrane electrolyte and the Pt, C/PBI (H_3PO_4)/Pt, C assembly (the working electrode area is 5 cm^2) were

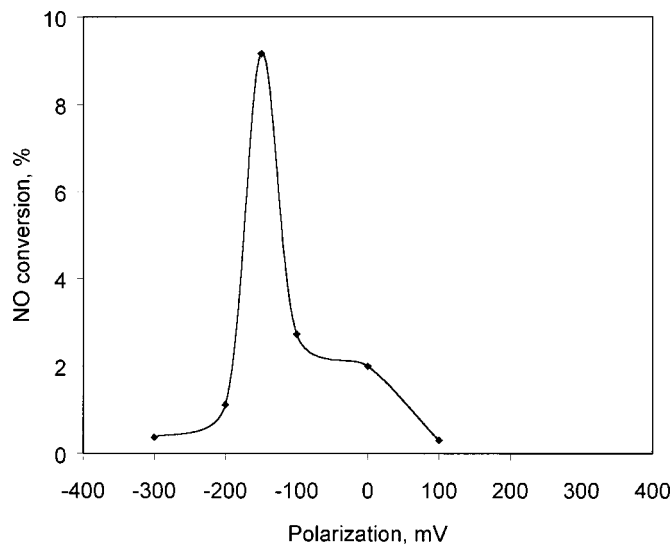


Figure 2. Dependence of NO conversion on polarization obtained in (NO, H_2 , Ar), Pt/polybenzimidazole (PBI)- H_3PO_4 /Pt, (H_2 , Ar) fuel cell at high NO + H_2 + Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure) and at 135°C .

developed in our group as well as by others.³ Graphite plates with gas channels were used as holders and current collectors. Two aluminum end plates with attached heaters were used to clamp the graphite plates. The temperature was controlled by a home-made controller. Mass flowmeters (5850 S Brooksmart) and 0154 Brooks Instrument controllers were used to control the inlet gas composition. The outlet gas composition was measured by an on-line quadrupole mass spectrometer (QMS 421, Pfeiffer) with a secondary electron multiplier detector and a cross-beam ion source with a rhenium filament. The ionization voltage was 70 V. The outlet gases were admitted to the mass spectrometer from the fuel cell through an 0.8 mm stainless steel capillary.

The mixture of NO and hydrogen, diluted by Ar ($\text{NO}/\text{H}_2/\text{Ar} = 17 \text{ mL/min}; 17 \text{ and } 354 \text{ mL/min}; \text{ or } 17 \text{ mL/min}; 17 \text{ and } 140 \text{ mL/min}$, respectively, at atmospheric pressure) was used as a working mixture at one electrode and hydrogen/argon mixture (H_2/Ar was 17 and 371 mL/min or 17 and 140 mL/min, respectively) was used as a reference and a counter gas at the other electrode. The temperature was $135\text{--}137^\circ\text{C}$.

Commercial gases NO (99.9%), H_2 (99.9%, $\leq 10 \text{ ppm of O}_2$, $\leq 15 \text{ ppm of H}_2\text{O}$), and Ar ($< 40 \text{ ppm O}_2 + \text{H}_2\text{O}$) were used.

An EG&G Instrument (Princeton Applied Research) 283 potentiostat/galvanostat controlled by 352 SoftCorr™ III Software was used for electrode polarization and steady-state voltammetric measurements. The initial (at zero polarization) catalytic activity was measured after the yield of gas products had stabilized, *i.e.*, under steady-state conditions. For each value of polarization the measurements were performed after stabilization of the yield of gas products (1-1.5 h). NO conversion vs. polarization curves were reproduced for each studied product and temperature. The open-circuit potential of the working electrode was approximately 0.14 V.

Results and Discussion

The results of the investigation of the electrochemical promotion of the catalytic NO reduction are given in Fig. 2-5. The presented data has been obtained at high and low gas flow rates to create the conditions where there are, respectively, an underproduction and an overproduction of the Pt-H_{ads} and $\text{Pt-H}_{\text{ads}}^+$ sites at the catalyst-gas interface through the chemical reaction.

Data in Fig. 2 and 3 were obtained at high gas flow rate after the catalyst was first polarized 0.1 V positively and then negatively to

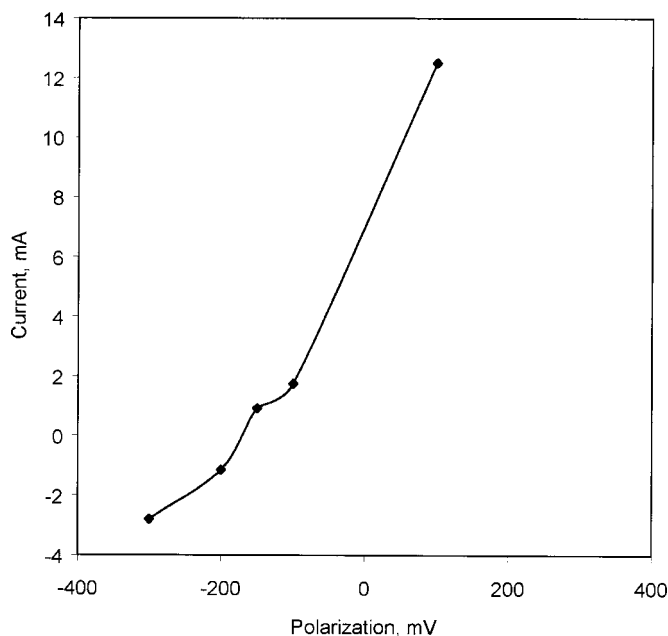


Figure 3. Steady-state voltammetric curve obtained at Pt catalyst at high NO + H₂ + Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure) and at 135°C.

−0.3 V. Nitrogen and water are the NO reduction products. Without polarization the NO conversion was 2% (Fig. 2). The reaction is assumed to be



Dependence of the NO conversion on polarization is given in Fig. 2. It can be seen that Reaction 6 can be electrochemically promoted at negative polarization and exhibits a clear “volcano”-type promotion behavior.⁶ This means that there is a maximum promotion effect (9.3% NO conversion) at a polarization of approximately −0.15 V, or −0.01 V catalyst potential vs. the reversible hydrogen electrode, RHE. The catalytic rate enhancement ratio at this maximum is 4.65. Figure 2 shows no NO conversion at a polarization ≤ 0.1 and ≤ -0.3 V.

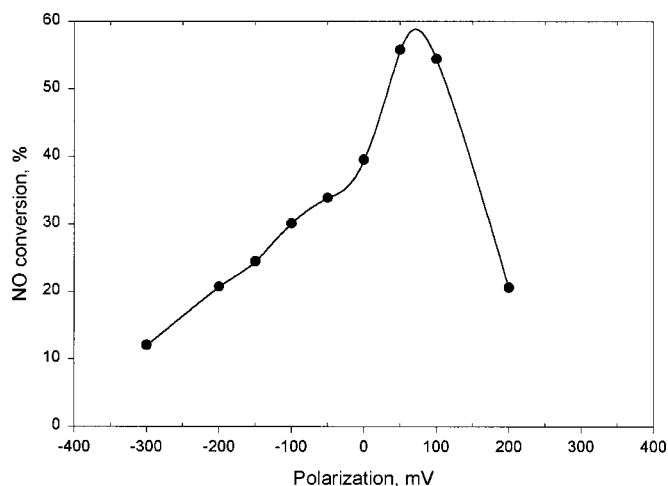


Figure 4. Dependence of NO conversion on polarization obtained in (NO, H₂, Ar), Pt/polybenzimidazole (PBI)-H₃PO₄/Pt, (H₂, Ar) fuel cell at low NO + H₂ + Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively, at atmospheric pressure) and at 135°C.

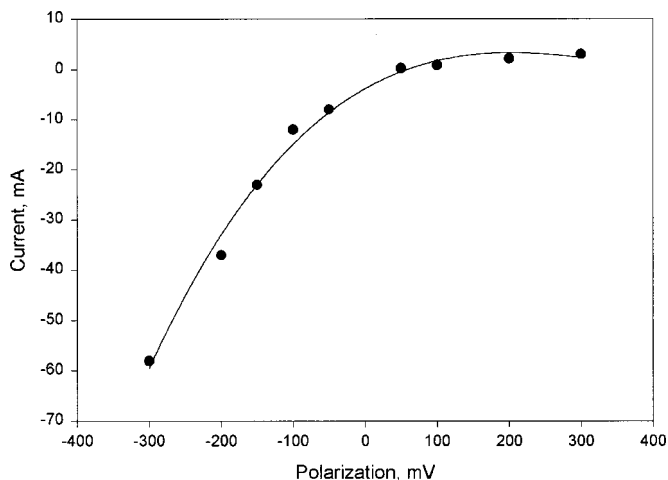


Figure 5. Steady-state voltammetric curve obtained at Pt catalyst at low NO + H₂ + Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively, at atmospheric pressure) and at 135°C.

There are obvious anodic and cathodic faradaic reactions inside this potential region (presence of the voltammetric waves, Fig. 3). The anodic current at the potential of maximum effect was 0.2 mA/cm². The value of Λ calculated for the maximum promotion effect was 1.26×10^3 , *i.e.*, $\Lambda \gg 1$. This means that this effect has an EPP nature.²

The closest published example of an electrochemically promoted catalytic reaction is the catalytic oxidation of CO by O₂ at the Pt catalyst on YSZ support.¹⁹ According to Belyaev *et al.*, this catalytic reaction is promoted by ZO₂[−] oxygen species which are the products of the interaction between electrochemically produced ZO[−] species and chemically adsorbed oxygen species Z_oO (where Z are the catalyst active sites at the catalyst-support-gas interface and Z_o are the catalyst active sites at the catalyst-gas interface). We can assume here that both electrochemically produced ZH and chemically produced Z_oH species, and also the possible product of their interaction with H⁺, ZH₂⁺, can promote the NO catalytic reduction. The reaction



takes place in the potential range between 0 and 0.4 V vs. RHE,²⁵ *i.e.*, at the potentials of the electrochemical promotion of NO reduction (Fig. 2). The nature of promotion of NO reduction by the adsorbed hydrogen species is probably the same as the nature of the promotion of the same reaction by the adsorbed Na atoms.^{11–14} It has been shown that the rate-determining step of the catalytic NO reduction at a Pt catalyst is dissociative chemisorption of NO because Pt is relatively ineffective at this step.²⁴ Adsorbed hydrogen species can act to increase the adsorption strength of electronegative adsorbates (NO) and weaken the N–O bond in the adsorbed molecule and therefore promote NO dissociation.¹³

Data in Fig. 4 and 5 were obtained at low gas flow rate after the catalyst was first polarized −0.3 V negatively and then positively to 0.2 V. It can be seen from comparison of Fig. 2 and 4 that NO reduction is increased 20 times even without polarization. Moreover, under these conditions negative polarization decreased the rate of NO reduction (*i.e.*, an opposite effect to what was found at high gas flow rates). It can also be seen that the electrochemical promotion effect did occur at a positive polarization with maximum increase at approximately 0.08 V polarization and with 1.5 times the zero polarization value.

The steady-state voltammetric behavior of the catalyst at a low gas flow rate is shown in Fig. 5. It is obvious from Fig. 5 that in the potential range of the promotion effect faradaic current is absent.

This means that the promotion effect has a CI nature.² Increase of the NO conversion under open-circuit conditions and changes in the nature of the promotion effect can be explained by a high concentration of Pt-H sites at the low gas flow rates. The increased number of the adsorbed hydrogen species (as in the NO promotion with Na^{12,24}) can complicate the NO (electronegative adsorbate) chemisorption, especially at negative polarization. At positive polarization, however, the charge-induced change of the strength of chemisorptive bonds can take place (CI effect).

Conclusions

The possibility of the electrochemical promotion of the catalytic NO reduction by hydrogen at the Pt-PBI(H₃PO₄)-gas boundary has been demonstrated. It has also been shown that the nature of this promotion effect can vary depending on the flow rate of the NO/H₂/Ar gas mixture. At high NO + H₂ + Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure), it has been found that NO reduction can be electrochemically promoted at negative polarization with maximum at approximately -0.15 V, *i.e.*, close to the potential found for the maximum promotion of CH₄ oxidation at the same catalyst.² The maximum rate enhancement ratio was 4.65. The value of Λ calculated for maximum promotion effect conditions was 1.26×10^3 , *i.e.*, $\Lambda \gg 1$. This means that this effect has an EPP nature, the catalytic reaction was promoted by the electrochemically produced adsorbed hydrogen species.

At low NO + H₂ + Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively, at atmospheric pressure), NO reduction increased 20 times even without polarization. Moreover, under these conditions negative polarization decreased the rate of NO reduction (*i.e.*, an opposite effect to what was found at high gas flow rates). However, the electrochemical promotion effect did occur at positive polarization with maximum increase at approximately 0.08 V and with 1.5 times the zero polarization value. In the potential range of the promotion effect faradaic current is absent. It means that the promotion effect has a CI nature. This means that the effect was caused by the charge-induced change of the strength of chemisorptive bonds.

Acknowledgments

This investigation has been supported by the PSO-F&U contract no. 3089 and by the Danish Research Councils ICAT project no. 9702636.

Technical University of Denmark assisted in meeting the publication costs of this article.

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