# *Zirconia potentiometric oxygen sensor activation using NEMCA*

Pavel Shuk and Robert Jantzt
Rosemount Analytical Inc., Process Analytic Division
Emerson Process Management
Solon, OH & Irvine, CA, USA
Pavel.Shuk@emerson.com

*Abstract*—**NEMCA known for the increasing the catalytic activity/selectivity of the gas exposed electrodes was investigated for the potentiometric zirconia oxygen sensor activation. Electrochemical promotion of $O_2$-sensors with Pt-cermet electrodes aged in the field was significant with up to 5 times in the impedance reduction. Stability test on the NEMCA activated $O_2$-sensors was showing just a minor impedance increase. Sensor response time was reduced by NEMCA effect by ~5-10% with up to 3 times signal noise reduction on the aged $O_2$-sensors.**

***Keywords-zirconia; potentiometric oxygen sensor; impedance; response; re-activation; NEMCA effect***

## I. INTRODUCTION

Electrochemical oxygen sensors based on zirconia solid electrolytes widely used today in different industrial applications and for the controlling fuel/air ratio in internal combustion engines (lambda sensor) were discovered in 1961 60th by Peters and Möbius [1] and Weissbart and Ruka (Westinghouse) [2]. Most industrial zirconia oxygen analyzers are based on the electrochemical sensor with stabilized solid electrolytes working in potentiometric mode [3-6] and after the exposure to the severe process high temperature environment will be degrading after months or years of service requiring more frequent sensor re-calibration/validation or even sensor replacement.

Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA), also known as Electrochemical Promotion Of Catalysis (EPOC) or In-Situ Controlled Promotion" (ICP) was first discovered in 80th by Costantinos G. Vayenas and is used to increase the catalytic activity (up to 90-fold) and selectivity of a gas exposed electrodes on a solid electrolyte cell upon application of a potential [7]. It was shown that electrochemistry can be used to activate and precisely tune heterogeneous catalytic processes with the catalyst supported by ionic or mixed ionic-electronic conductors. These materials can act as reversible in situ promoter donors or poison acceptors to affect the catalytic activity and selectivity of the electrodes deposited on the solid electrolytes. This phenomenon was well documented and has been observed on the various electrode surfaces, e.g., Pt, Ni, Au and Pd supported by $O^{2-}$, $Na^+$ and proton conductive solid electrolytes for the different catalytic reactions [8-14]. This electrochemical promotion is due to the potential- or current-controlled electrocatalytic Faradaic introduction of the catalysis promoting species, e.g., $O^{2-}$, $Na^+$ or $H^+$ from the ionic conductive solid electrolyte to the catalyst/gas interface. This non-Faradaic activation of heterogeneous catalytic reactions is a promising application of the electrochemistry with several technological possibilities, particularly in industrial catalyst product selectivity modification and in exhaust gas treatment [15]. Non-Faradaic electrochemical modification of catalytic activity known for the increasing the catalytic activity and selectivity of the gas exposed electrodes was investigated for the first time in new and 'aged' industrial $O_2$-sensors electrochemical activation affecting the sensor response, impedance and stability.

## II. EXPERIMENTAL

Industrial zirconia potentiometric oxygen sensors (12 "aged" and 37 new) were evaluated on the impedance test rack as well in the 6888 $O_2$ Analyzer (Fig. 1) for the response, reproducibility and stability. After stabilizing the temperature at 736°C the cell impedance was measured using Digital Multimeter Fluke 87 III (Fluke, WA) before and after NEMCA treatment. The impedance measurements of the selected "aged" $O_2$ cells were carried out using Solartron 1260 Frequency Analyzer (Solartron Analytical Corp, UK) in 0.1Hz…10MHz frequency range. Optimized ~1.5 V DC was applied to the cell's electrodes for 1, 3 or 5 min using Precision DC Source Model 2020B (Power Designs Inc., NY).


Figure 1. 6888 $O_2$ Analyzer with $O_2$-sensor mounted on the probe end

Test gas mixtures were prepared using calibrated Environics 4000 mixing system (Environics, Inc., CT) and mixed oxygen concentrations were certified using a calibrated 6888 $O_2$ Analyzer (Rosemount Analytical Inc., OH). The gas flow rate was kept constant at 2.5 L/min. The gas concentration was varied between 2 and 20% $O_2$. Data acquisition system from National Instruments including signal conditioning module (SCXI-1000+SCXI-1102 card) and the plug-in DAQ card (AT-MIO-16 XE-50) was used for the raw signal sensor data collection.

## III. RESULTS AND DISCUSSION

As expected no significant NEMCA effect was observed on already chemically activated new $O_2$-sensors with just 5…30% sensors impedance reduction (Figs. 2-3). Short ~1 min NEMCA treatment was sufficient and the activation effect was quite permanent with the slight impedance degradation starting in ~2 weeks. NEMCA treatment on "aged" oxygen sensors exposed for 1-2 years to the combustion process flue gas was significantly increasing Pt-electrodes activity with the cell impedance up to 10 times reduction except for not degraded low impedance (<100 Ω) $O_2$-sensors in Fig. 4.

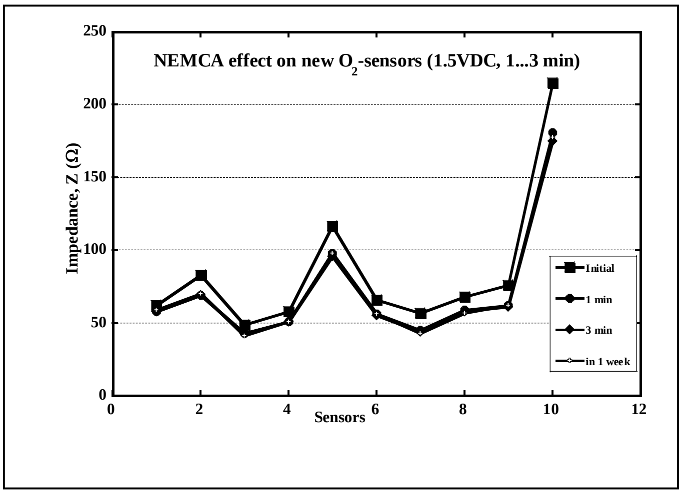


Figure 2. NEMCA effect on new and 'aged' $O_2$-sensors at 736°C

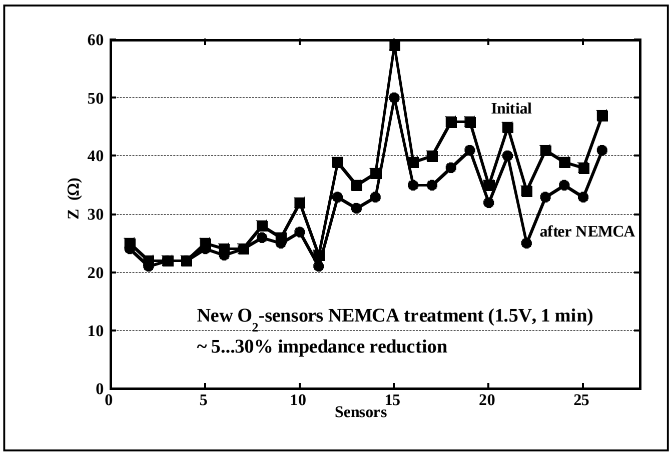


Figure 3. NEMCA effect on new $O_2$-sensors at 736°C

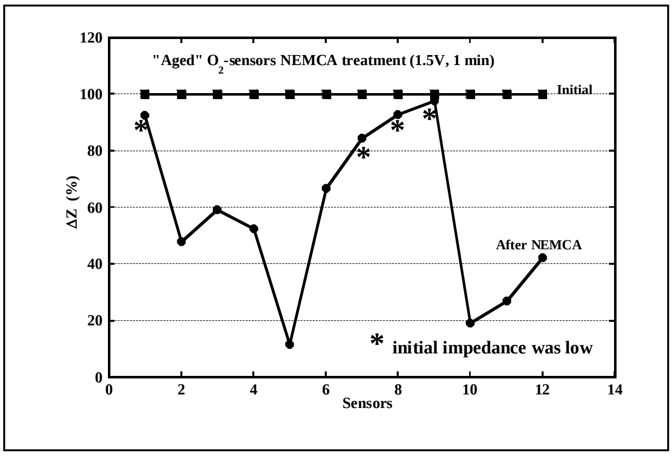


Figure 4. NEMCA effect on "aged" $O_2$-sensors at 736°C

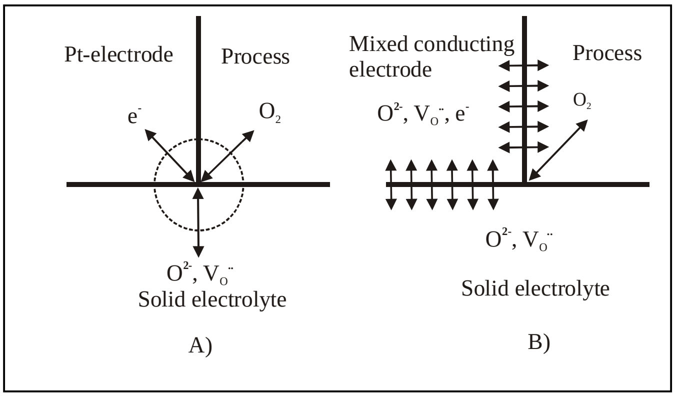


Figure 5. Oxygen sensor electrochemical reaction chematically [16]

The oxygen reaction in the electrochemical oxygen sensor (Fig. 5A) is taking place on the triple phase boundary (TPB: electrode, electrolyte, and gas) where the oxygen molecules ($O_2$), electrons (e') and oxygen vacancies ($V_O^{\cdot\cdot}$) are available and with the elemental steps of the reaction including molecular oxygen diffusion in the gas phase and absorption (1), diffusion and dissociation on the electrolyte/electrode surface (2), diffusion to TPB (3) and final oxygen electrochemical reaction (4):

$$O_2(gas) \leftrightarrow O_2(electrolyte/electrode) \quad (1)$$

$$O_2(electrolyte/electrode) \leftrightarrow 2O(electrolyte/electrode) \quad (2)$$

$$2O(electrolyte/electrode) \leftrightarrow 2O\ (TPB) \quad (3)$$

$$2O(TPB)+4e'(electrode)+2V_O^{\cdot\cdot}(electrolyte) \leftrightarrow 2O_O \quad (4)$$

By using mixed ionic-electronic conductive electrode or cermet electrode with electronic and ionic conductors, e.g., Pt-zirconia, the oxygen electrochemical reaction will be expanding to the electrode bulk (Fig. 5B) improving the electrode performance like was used in this study. The electrochemically active sites are assumed to be in the vicinity of the three-phase boundary [17] and NEMCA of the Pt- or Pt-cermet electrode most likely will be improving the critical electrochemical step of the oxygen reaction.

As it can be seen from Fig. 6 the NEMCA effect is quite permanent on the new $O_2$-sensors with the impedance starting to increase in 1…2 weeks on the “aged” $O_2$-sensors but still remaining by 50…100% well under the initial impedance value before the NEMCA treatment.

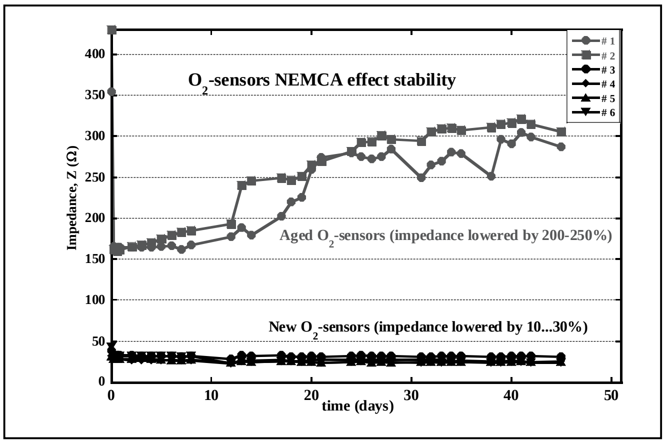


Figure 6. $O_2$-sensors impedance stability after NEMCA treatment at 736°C

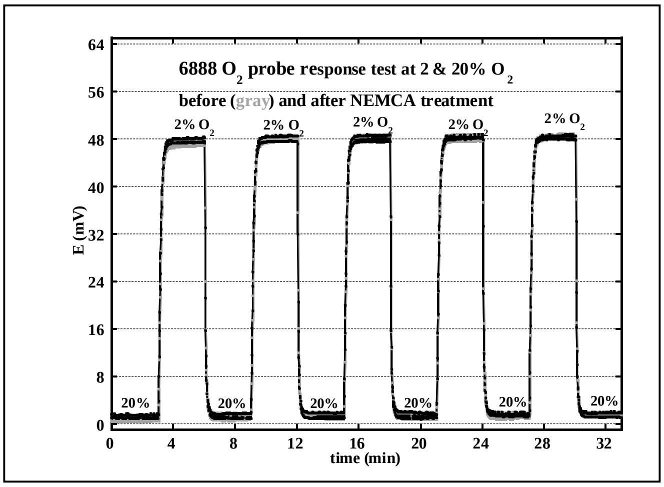


Figure 7. NEMCA effect on aged” $O_2$-sensor response to 2/20% $O_2$ at 736°C

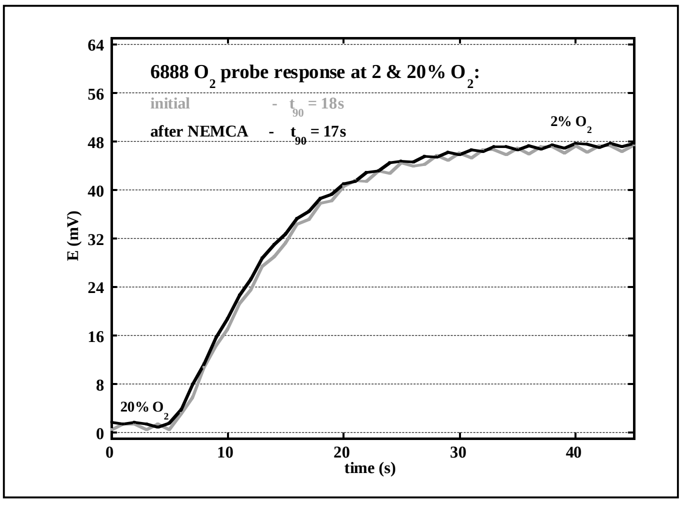


Figure 8. NEMCA effect on new $O_2$-sensor response to 2% $O_2$ at 736°C

The response time and stability of the oxygen sensor after the NEMCA treatment was slightly improved even on new already chemically activated sensors (Figs. 7-8) with the significant raw mV sensor signal noise reduction on the “aged” $O_2$-sensors (Fig. 9). Most likely it was attributed to the smooth electrochemical reaction path on triple gas/electrode/electrolyte boundary after the NEMCA treatment “cleaning the electrode

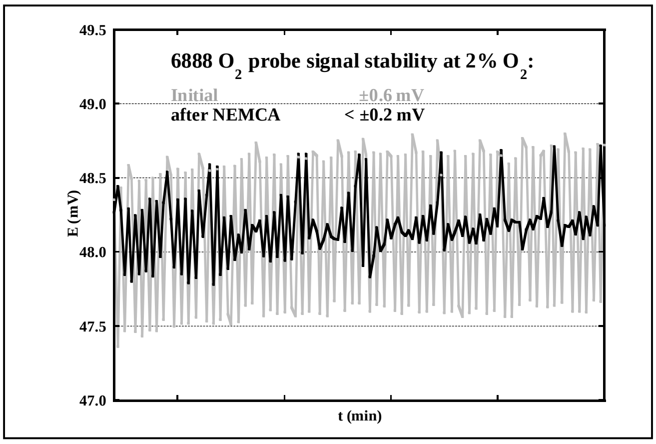


Figure 9. NEMCA effect on the “aged” $O_2$-sensor signal noise at 736°C

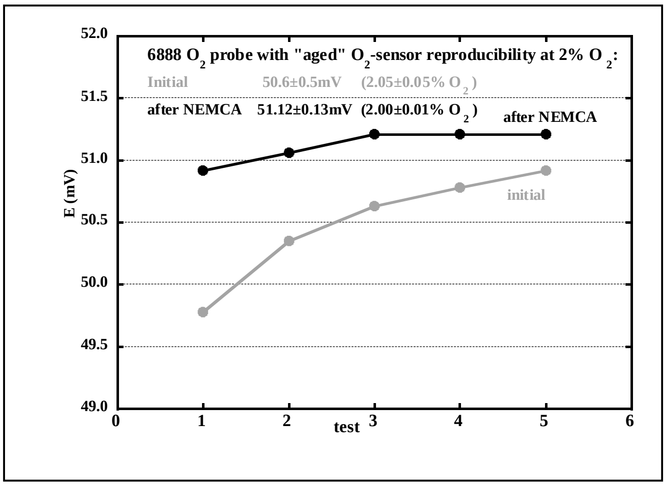


Figure 10. NEMCA effect on the “aged” $O_2$-sensor reproducibility at 2% $O_2$

reaction zone”. The sensor reproducibility was highly improved from initial ±0.05% $O_2$ to ±0.05% $O_2$ at ~2.0% $O_2$ concentration after NEMCA treatment (Fig. 10).

Further investigations on the NEMCA effect stability in the long term and the effect reliability on the zirconia oxygen sensors operating in severe combustion environment would be required to define the NEMCA application perspective and limits.

## IV. Conclusion

NEMCA effect known for the increasing the catalytic activity/selectivity of the gas exposed electrodes for the first time was investigated on the potentiometric oxygen sensors. Electrochemical promotion on $O_2$-sensors with Pt-cermet electrodes was significant especially on the sensors aged in the field bringing up to 5 times sensor impedance reduction. The NEMCA effect was also notable on $O_2$-sensor raw signal reducing 90% response time by 5-10% and up to 3 times the signal noise of the aged oxygen sensors. Stability test on the NEMCA activated $O_2$-sensors was showing just a minor impedance increase after 2 weeks with the accelerated impedance degradation on the aged sensors.

## ACKNOWLEDGMENT

The authors would like to thank Rosemount Analytical Inc. supporting this research program and Professor Costantinos G. Vayenas as well as Dr. Susanne Brosda for the sharing numerous NEMCA publications and NEMCA/EPOC/ICP knowledge.

## REFERENCES


[1] H. Peters and H.-H. Möbius, "Procedure for the gas analysis at elevated temperatures using galvanic solid electrolyte elements", DD-Patent 21673, August 1961.

[2] J. Weissbart and R. Ruka, „Oxygen gauge", Rev. Sci. Instrum., vol. 32, pp. 593-595, May 1961.

[3] H.-H. Möbius, "Solid state electrochemical potentiometric sensors for gas analysis", in Sensors a comprehensive survey, vol. 3, W. Göpel, J. Hesse, J. N. Zemel, Eds. New York: VCH, pp. 1105-1154, 1992.

[4] W. C. Maskell, "Progress in the development of zirconia gas sensors", Solid State Ionics, vol. 134, p. 43-50, January 2000.

[5] S. Zhuiykov, Electrochemistry of zirconia gas sensors, Boca Raton/London/New York, CRC Press, 2008.

[6] P. Shuk, "Process zirconia oxygen analyzer: state of art", Technisches Messen, vol. 77, No 1, pp. 19-23, January 2010.

[7] C. G. Vayenas, S. Bebelis, S. Neophytides, "Non-Faradaic electrochemical modification of catalytic activity", J. Phys. Chem., vol. 92, pp. 5083-5085, N 18, 1988.

[8] C. G. Vayenas, S. Bebelis and S. Ladas, "Dependence of catalytic rates on catalyst work function", Nature, vol. 343, pp. 625-627, February 1990.

[9] Y. Jiang, I. V. Yentekakis and C. G. Vayenas, "Methane to ethylene with 85 percent yield in a gas recycle electrocatalytic reactor-separator", Science, vol. 264, pp. 1563-1566, June 1994.

[10] C. G. Vayenas and S. I. Bebelis, "Electrocatalysis, catalysis and electrochemical promotion in solid electrolyte cells", in Oxygen ion and mixed conductors and their technological applications, H. L. Tuller, J. Schoonman, I. Riess, Eds. Dordrecht-Boston-London, Kluwer Academic Publishers, 2000, pp. 123-164.

[11] C. G. Vayenas, S. Bebelis, C. Pliangos, S Brosda and D. Tsiplakides, Electrochemical activation of catalysis: promotion, electrochemical promotion, and metal-support interactions, Kluwer Academic, New York, 2001.

[12] C. G. Vayenas, A. Katsaounis, S. Brosda and A. Hammad. "Electrochemical modification of catalytic activity", in Handbook of Heterogeneous Catalysis, vol 8, G. Ertl, H. Knözinger, F. Schüth and J. Weitkamp, Eds. Weinheim, Wiley-VCH Publishers, 2007, pp. 1905-1935.

[13] A. Katsaounis, "Electrochemical promotion of catalysis (EPOC) perspectives for application to gas emissions treatment", Global NEST, vol. 10, pp. 226-236, February 2008.

[14] C. G. Vayenas and C. G. Koutsodontis, "Non-Faradaic electrochemical activation of catalysis", J. Chem. Phys., vol. 128, 182506, pp. 1-13, 2008.

[15] C. G. Vayenas: "Bridging electrochemistry and heterogeneous catalysis", J. Solid State Electrochem., vol. 15, pp. 1425-1435, March 2011.

[16] P. Shuk, E. Bailey, U. Guth, "Zirconia oxygen sensor for the process application: state-of-the-art", Sensors & Transducers Journal, vol. 90, pp. 174-184, April 2008.

[17] K. Kinoshitta, Electrochemical oxygen technology, John Wiley & Sons, New York-Chichester-Brisbane-Toronto-Singapore, 1992.