

## Voltage – Concentration Relations with Enhanced Slopes in Electrochemical Cells Based on Nafion<sup>®</sup>

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In electrochemical cells based on Nafion<sup>®</sup>, exposed to a humid atmosphere, that contains oxygen, hydrogen or a mixture of oxygen and hydrogen, the open circuit voltage,  $V_{oc}$ , depends on the driving forces generated by gradients in the concentrations  $[H_2]$  and  $[O_2]$  in the gas phase. When the gas composition is fixed at one electrode the open circuit voltage varies linearly with the logarithm of the hydrogen concentration as,

$$V_{oc} = n \frac{k_B T}{2q} \ln[H_2] + \text{constant}, \quad [1]$$

and  $n=1$  and with the logarithm of the oxygen concentration as,

$$V_{oc} = n \frac{k_B T}{4q} \ln[O_2] + \text{constant} \quad [2]$$

and  $n=1$ . We have observed in cells of the form Pt/Nafion/Ag and Pt/Nafion/Pd, a different behavior with  $n$  different from unity, having values either significantly higher than unity ( $n \sim 6$ ) or zero (1), as also observed by others (2-5).

Two explanations have been given to the enhanced slope ( $n > 1$ ). First, the mobile charged specie in Nafion<sup>®</sup> is a complex consisting of a proton and solvating water molecules in the form

$H^+ \bullet (H_2O)_m$ . Therefore the coefficient  $n$  can be different from unity when there is an additional driving force due to a gradient in the water concentration, as this also drives  $H^+ \bullet (H_2O)_m$  (2-4). However in our experiments the water concentration is kept uniform (and the same in all measurements) and no additional driving force is expected if the water reacts with the Nafion<sup>®</sup> and electrodes under equilibrium conditions. Muira et al. (5) have also observed a slope with  $n$  higher than unity. They suggested a different explanation, that the enhanced slope is due to a mixed potential formed by the oxidation of hydrogen. However this explanation

cannot be applied when one of the reacting gases  $H_2$  or  $O_2$  is missing.

We suggest a different explanation that involves reactions that are in equilibrium and others totally blocked<sup>1</sup>. With this mixed equilibrium-non equilibrium approach (MENEA) we are able to interpret all the experimental results obtained under different conditions. In the analysis of these experiments we always find a water transference coefficient  $m \sim 3$ , as expected for the specie  $H^+ \bullet (H_2O)_m$  in highly humidified Nafion<sup>®</sup>. The explanations are consistent with: a) Ag and Pd catalyzing the absorption of water by Nafion<sup>®</sup>, b) Pt and Pd catalyzing the reaction of oxygen and hydrogen with charged complexes in Nafion<sup>®</sup>, and c), that, in the absence of oxygen, Ag, Pt and Pd form an oxide by reaction with water.

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