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Hydrogen Evolution on Ni Electrode during Synthetic Tap Water Electrolysis

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1 Introduction

Electrolysis is a key technology in the production of hydrogen from renewable sources, especially those that generate electricity, such as solar, wind and hydroelectric power. While hydrogen producing electrolysers are industrially available [1, 2], these are especially aimed at the production of hydrogen as a chemical, not as an energy carrier. For the large scale application of hydrogen as an energy carrier for automotive applications, the hydrogen cost, energy efficiency of the electrolyser and the resulting hydrogen quality are key factors that need more attention. The need for ultrapure water in the present generation electrolysers is another factor that contributes to cost and hinders widespread introduction.

The current research attempts to investigate the influence of the contaminants in the tap water on the hydrogen as well as oxygen evolution reaction (HER/OER) on Ni electrodes.

2 Experimental

The electrochemical set up used in this study was three electrode Pyrex glass cell employing a large platinum basket as CE (counter electrode), a solid Nickel cylindrical electrode as WE (work electrode), and a reference electrode (RE) connected to the cell by a bridge allowing to keep the RE at room temperature. The solutions were prepared from p.a. grade chemicals and distilled 18 $M\Omega.cm^{-2}$ water, with 1 $mol.dm^{-3}$ KOH added to increase the conductivity. The synthetic tap water was prepared by different salts in the proper concentration according to the recipe obtained from a water monitoring laboratory in the Netherlands (N. V. PWN Waterleidingbedrijf Noord-Holland, location Bergen) [3]. The electrochemical equipment used was a Solartron SI 1287 electrochemical interface coupled with FRA SI 1255 frequency response analyzer. The temperature of the cell was controlled by a thermostat with accuracy within $\pm 1\ C^{o}$. The gas phase was analyzed by a gas-chromatograph while the electrode surface structure was studied with the help of scanning electron-microscope using SEM and EDX techniques.

3 Results and Discussion

Fig 1. shows the steady-state polarization curves of the Ni electrode in 1 $mol.dm^{-3}$ KOH pW and sTW at 298 and 353 K for HER. The difference in the performance between the two media is due to the influence of the impurities in the sTW on the electrode kinetics. As the WE in the case of HER is negatively charged only cations may take part in the electrochemical reaction at the electrode/electrolyte interface. However, it is known that anions, especially those from the halogen elements group, can undergo chemical adsorption on the electrode surface under similar conditions. As result they block the active sites of the WE where the electrochemical reaction occurs. In such case, at identical current densities the potential of the partially covered with chemisorbed species WE will be higher. On the contrary, at one and the same potential the current density of WE will be lower.

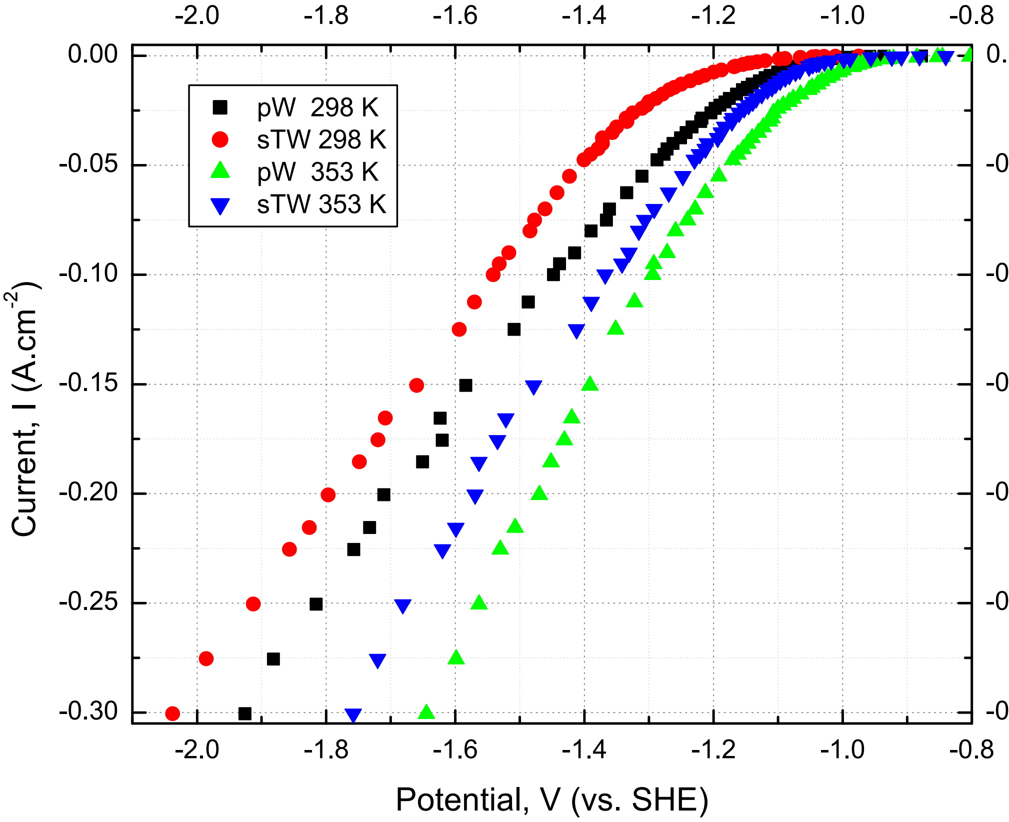

Figure 1: **Polarization curves of Ni electrode in 1 mol.dm^{-3} KOH pure water (pW) and synthetic tap water (sTW) at two different temperatures.**

Fig. 2 shows the SEM images of the WE surface composition after polarization tests. The results from EDX analyses are summarized in Table 1. The presence of Cl, S, Na, Mg as well as the higher content of C and O in the case of sTW can only be attributed to their presence in the bulk electrolyte as impurities. As expected, the latter two elements are also identified for pure water, because CO_2 from the air is easily dissolved in an alkaline solution.

Table 1: **Quantified results from the EDX spectrum from Fig.2.**

Weight %	C	O	Na	Mg	Si	S	Cl	K	Fe	Zn	Pb	Ca	Cr	Ti	Ni
pW	8.44	6.61			0.92			0.11	7.43		0.86	0.06	0.06	0.13	75.27
sTW	39.82	15.39	2.97	0.03	1.13	0.25	2.19	3.00	28.73	1.7	4.78				

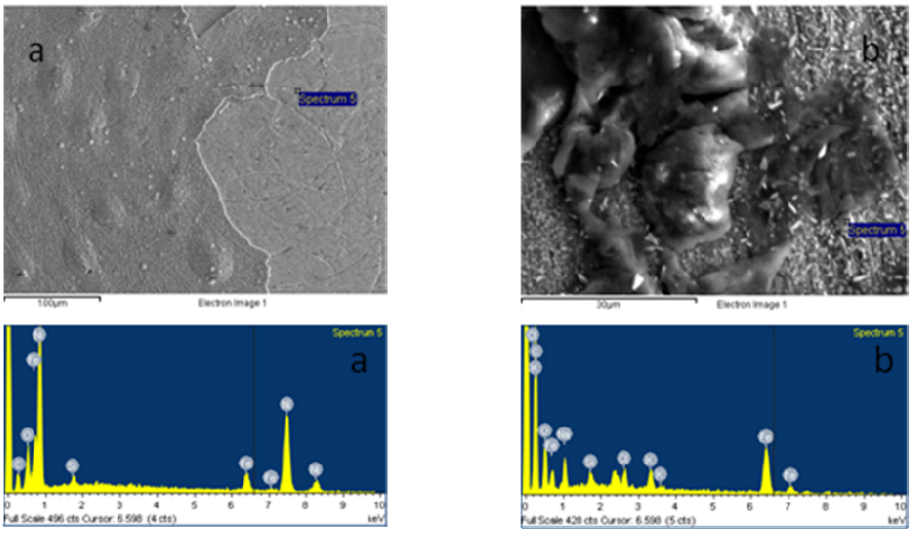

Figure 2: **SEM and EDX spectrum images of Ni electrode after steady-state polarization in a) pure water + 1 mol.dm^{-3} KOH, b) synthetic tap water + 1 mol.dm^{-3} KOH.**

Electrochemical Impedance Spectroscopy (EIS) measurements show that the systems under study display only one semi-circle in the impedance complex-plane, which is slightly distorted (Fig. 3). EIS complex-plane plots were approximated through R_s/CPE/R_{ct} equivalent circuit, where R_s represents the solution resistance, R_{ct} is the charge-transfer resistance related to the electrode kinetic and CPE is a frequency dependent parameter used instead of C_{dl} - pure double layer capacitance in case of surface inhomogeneities. Only R_{ct} gives information about the electrochemical rate of the reaction – the smaller the value of the R_{ct} the higher the rate is. This can be easily recognized on Fig. 3 since R_{ct} is defined in general as the diameter of the semi-circle [4]. R_{ct} of pure water is smaller compared with the sTW system which is in good agreement with the polarization measurement results.

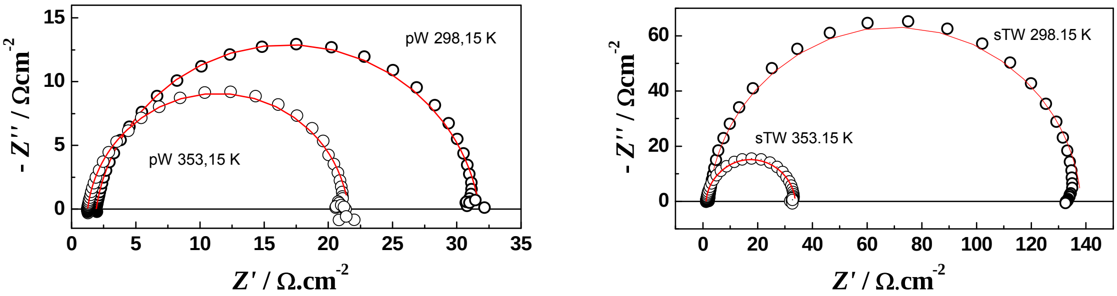

Figure 3: **Complex-plane plots of Ni electrode in pure (pW) and synthetic tap water (sTW) at 298 and 353 K at constant potential -1.022 V vs. SHE.**

The existence of only one semi-circle in both cases also indicates that the impurities in sTW do not participate in the charge-transfer reaction. If a $\log 1/R_{ct}$ is plotted against E, it should yield a slope identical to the one obtained from steady-state curves. This is shown on Fig 4. The small difference in the values of the Tafel slope at one and the same temperature suggests that the mechanism of HER in sTW is the same as in pW within the potential region under investigation.

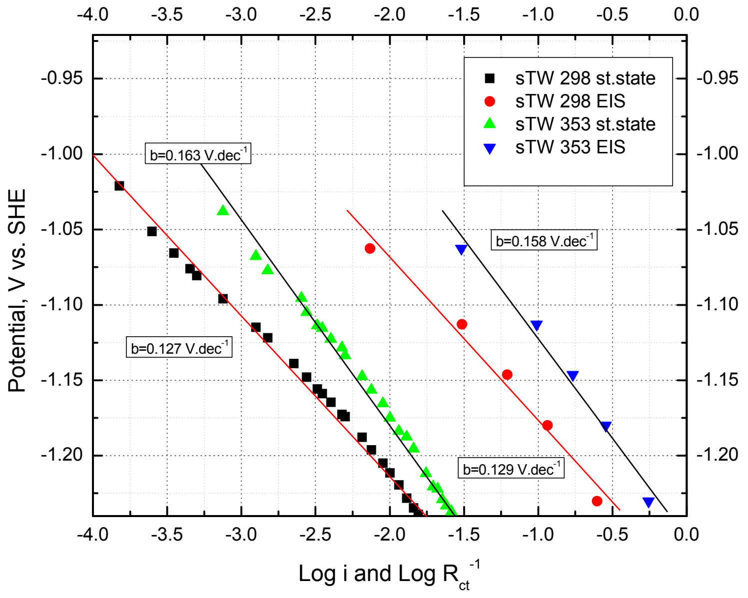

Figure 4: **Comparison of the Tafel slopes obtained from steady-state and EIS techniques in sTW at 298 and 353 K.**

The steady-state measurements usually cannot account for the stability of the system's performance with time. That is why long-term stability tests are performed to check the deviation of the parameters of interest under continuous operation conditions.

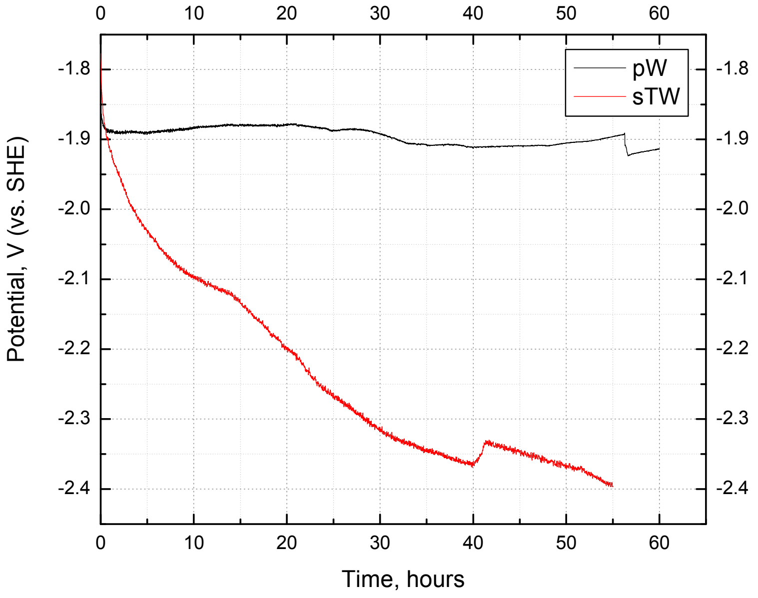

Figure 5: **Stability test for Ni electrode in 1 mol.dm^{-3} KOH pure water (pW) and synthetic tap water (sTW) at 298 K and constant current density of 0,25 A.cm^{-2}.**

Fig. 5 shows the performance of the Ni electrode in pW and sTW under polarization at a constant current of 0.25 A.cm^{-2} within 55 hours. In the case of pW the potential quickly reaches a steady value and remains almost unchanged for the whole period. This behaviour is not observed for sTW, whose potential continuously moves to more negative values. This fact could be due to the formation of $Ca(OH)_2$ or $Mg(OH)_2$ precipitates on the electrode surface. It is known that at pH higher than 10.7~11 Mg^{2+} or Ca^{2+} ions, if present in the solution, tend to form scales at the metallic surface of the electrode and later grow onto neutral surfaces in the form of hydroxides [5].

For the practical application on an electrochemical process it is important to lower the cost of the process itself and also to keep all other costs as low as possible for obtaining minimum price end products of interest. In this manner the purity of the products obtained is of great importance.

Using a gas-chromatograph attached directly to the electrochemical cell an attempt was made to analyze the gas phase for the most likely gases expected i.e. H_2, O_2, CO_2, CO, SO_x, NO_x, N_2 and H_2S. It has to be noted that no additional attempt to separate the anodic and cathodic compartments of the cell was made except that a glass tube positioned around the WE was mounted on the cell top thus allowing the formed gas bubbles to leave the cell body. In this manner gases evolved from the WE were driven to the gas-chromatograph and analyzed. With this experimental setup the quantity of the hydrogen obtained at 0.5 A.cm^{-2} is ca. 94~95% and 93% the latter being the result from sTW (Fig. 6). The rest is a mix of an O_2 and N_2. What is worth noting is that only CO_2 was detected in quantity in the range under 0.02 %V. No traces of CO which is known to play the crucial role in poisoning PEMWE electro-catalysts were detected.

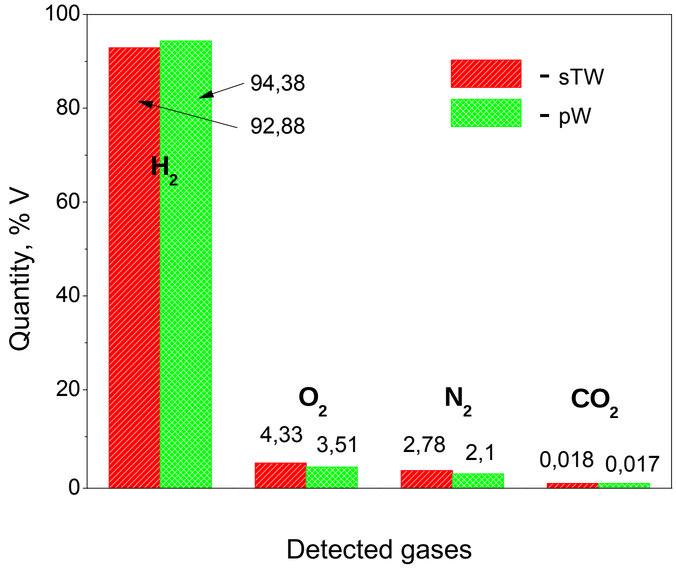

Figure 6: Gas analysis results.

Using the same experimental procedures Oxygen Evolution Reaction (OER) was also investigated. The experimental findings are discussed in details in the presentation.

4 Conclusion

The obtained results lead to the conclusion that impurities contained in synthetic tap water undergo chemical adsorption on the WE surface and block the active sites for the electrochemical reaction (HER) resulting in increased energy consumption. They do not take part in the electrochemical reaction whose mechanism seems to be the same in both media (pW and sTW). The purity of the obtained gas product at identical experimental conditions is almost equal. No stable potential was registered during the stability test within 55 hours which is probably due to additional formation of deposits on the WE surface. Having in mind all the above conclusions synthetic tap water electrolysis could enable energy storage in distributed off-grid application by simple conversion of available water using intermittent, renewable electricity.

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