



## Electrochemical Performance of Fe-Cr-Ni Electrode as Cathode for Hydrogen Evolution in KOH Solutions

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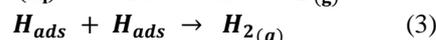
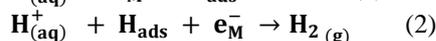
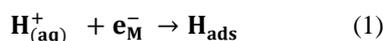
### Abstract

Electrocatalytic behavior of commercially available Fe-17Cr-14Ni alloy as a cathodic material for the evolution of hydrogen in alkaline solutions has been characterized by means of microstructural and electrochemical techniques. The microstructure of the alloys was examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. The electrochemical behavior of the examined materials was studied through potentiodynamic polarization techniques and electrochemical impedance spectroscopy (EIS). The effect of electrolyte concentration on the hydrogen evolution reaction (HER) rate and the cathode's electrochemical stability were studied. Tafel extrapolation method was used to determine the kinetic parameters characteristic of the hydrogen evolution reaction. The results show that the investigated alloy can be seen as a good candidate for large-scale and long-term hydrogen evolution. The rate of evolution of hydrogen under low overpotential is relatively high.

**Keywords:** EIS; Electrocatalyst; Fe-Cr-Ni Alloy; HER; Polarization.

### 1. Introduction

Sustainable, renewable fuel for the near future is urgently needed to save our world due to the depletion of fossil fuel and environmental pollution. Hydrogen (H<sub>2</sub>) is attractive and promising for oil, due to its high energy density and zero greenhouse gas emissions [1,2]. Electrocatalytic water splitting receives significant interest relative to other solutions to hydrogen production (e.g., steam reform, coal gasification), due to its technical simplicity and ecological cleanliness, lower costs, and fair efficiencies. The electro-adsorption/desorption of hydrogen, electro-dissociation/combination of hydrogen and chemical desorption are three main reactions involved in Hydrogen Evolution Reaction (HER), named Volmer's reaction (eq. 1), Heyrovsky's reaction (eq. 2) and Tafel's reaction (eq. 3) respectively [3].



The reaction to the evolution of hydrogen is usually carried out in the basic [4] and acidic media [5,6]. Nevertheless, the use of acidic electrolysis for the development of hydrogen remains limited by the high cost of proton exchange membranes used in an electrolyzer device and poor stability caused by corrosion problems [7]. Hence, the water electrolysis industry focuses primarily on enhancing HER's performance in the basic setting by choosing suitable electrode materials to decrease the hydrogen overpotential and to increase the rate of HER. The voltage used at broad current densities depends on the over-potential HER. Exceptional electrocatalytic activity, good electrical conductivity, long-term stability during the electrolysis process and high corrosion resistance are the typical qualities of the

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material used as a suitable candidate for hydrogen production. Metals and compounds based on platinum are normally seen as the perfect HER catalysts [8, 9]. But these noble metal-based electrocatalysts high cost and insufficiency severely restrict their wide-spread use in sustainable energy conversion systems [10]. In recent years, numerous investigations have focused on the preparation of new electrode materials with high electrocatalytic activity for the hydrogen evolution reaction [11-15]. As a possible substitute for noble metal catalysts, FeCr<sub>17</sub>Ni<sub>14</sub> alloy has attracted attention due to its abundant reserves and easy processing. Stainless steel, which is widely used as a conductive material for electrocatalysis and energy storage and due to its high durability and low cost, is a representative alloy material rich in transition metals such as Ni, Fe and Cr [16]. In recent time, stainless steel was, besides nickel alloys found to be particularly suited for cathode/anode pairs in water electrolysis systems [17]. The current work concerns the electrocatalytic behavior of commercial alloy Fe-17Cr-14Ni at 298 K as a catalyst for the HER. The objective is to use this alloy as a promising cathode for the evolution of hydrogen at lower over-potential hydrogen in various concentrations of KOH solution. In this regard, the HER's kinetics on these electrode materials was analyzed using spectroscopy measurements of steady-state polarization and EIS. Phase analysis of the samples before their electrochemical characterization was performed to establish a connection between microstructural characteristics and alloy electrocatalytic efficiency.

## 2. Experimental

Before the electrochemical measurements, the surface morphology and elemental composition of the alloy were investigated before immersion in the alkaline solution by using Scanning Electron Microscopy (SEM). Phase analysis of all samples was performed to test the structure, homogeneity of alloys. The metallographic research was performed on samples using standard methods and was dry-polished. The metallographic analysis was performed on samples, dry-polished using standard methods. ZEISS Gemini SEM-field emission scanning electron microscope with an EDX application and working at a 20 kV acceleration was used for the investigation, characteristics of the alloy. The freshly prepared KOH solution was prepared with distilled water using KOH Merck (Darmstadt,

Germany). Freshly prepared KOH solutions of different concentrations (2.0-0.01M) were used as test electrolytes.

The commercially available alloy Fe-17Cr-14Ni has used as a test specimen in spectroscopic tests. An electrochemical cell with three electrodes where the working electrode is the tested alloy with a surface area of 0.20 cm<sup>2</sup>; a saturated calomel electrode (SCE) is the reference electrode; and a platinum wire used as the counter electrode was used in the measurements. The working electrodes were scraped away before each trial using sequential grades of emery papers down to 2000 grit and polished with a soft cloth until it gained a bright-mirror appearance then washed with distilled water and transferred quickly to the electrolytic cell. Electrochemical of both spectroscopy and potentiodynamic polarization was calculated. A Voltalab PGZ 100 "All in one" potentiostat/galvanostat system was used to perform the polarization experiments and electrochemical impedance spectroscopic (EIS) investigations. The saturated calomel electrode, SCE, (0,245 V versus normal hydrogen electrode, NHE), has been used for calculating the working electrode potentials. A 10 mV s<sup>-1</sup> scanning rate was eventually developed to assess potentiodynamic polarization for anodic and cathodic polarization. Impedance tests in the range of frequency 0.1-10<sup>5</sup> Hz with the over-10 mV peak to peak AC signal were recorded.

## 3. Results and discussion

### 3.1. Physical Characterization

Figs. 1 (a, b) shows the SEM image and the XRD pattern of investigated polished commercially Fe-17Cr-14Ni alloy. SEM analysis (Fig. 1a) has been utilized to examine the surface morphology of the investigated alloy before the immersion in test electrolyte. Fig. 1b displays the XRD pattern of the commercial stainless steel alloy. From the XRD patterns, It can be noticed that the peaks obtained for the stainless steel confirm a single phase of austenite (pure face-centered-cubic, FCC with unit cell parameters  $a=1.199 \text{ \AA}$ ) which indicate the single-crystalline alloys. The average grain size of austenite is 19.10 nm in Fe-17Cr-14Ni.

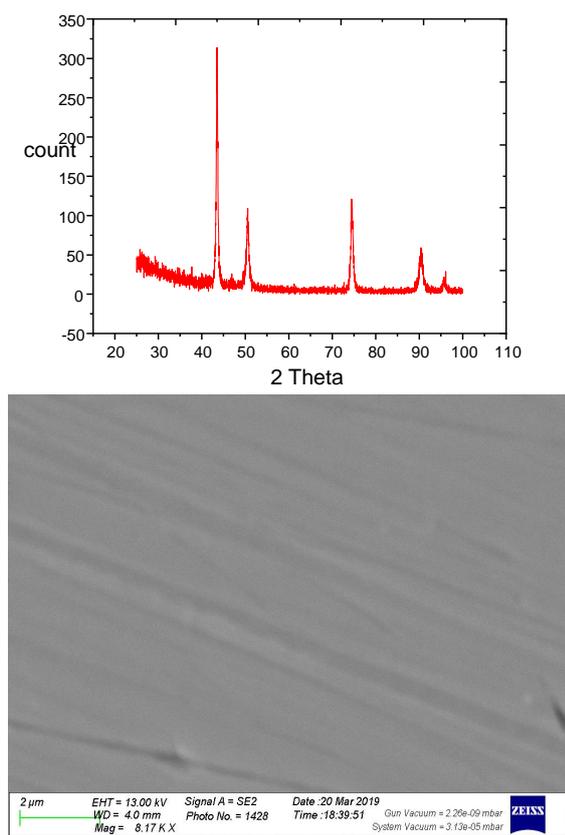


Fig. 1- SEM and XRD images of Fe-17Cr-14Ni stainless steel sample before immersion in test electrolyte.

### 3.2. Electrochemical Measurements

#### 3.2.1. Potentiodynamic polarization tests

An HER electrocatalyst's catalytic activity can always be evaluated employing potentiodynamic polarization tests [13, 18]. In KOH solutions of varying concentrations (2.0 - 0.01 M), the electrocatalytic performance of Fe-17Cr-14Ni alloy as a cathode material in terms of HER has been studied. The findings from Fig. 2 were set out in Table 1 which shows that with the negative shift in the electrode potential, the current density of the cathode increased rapidly. The similarity of the cathodic potential with the current in the linear Tafel region can be identified as in equation (4):-

$$\eta_c = \frac{2.3RT}{(1-\alpha)F} \log j^0 + \frac{2.3RT}{\alpha F} \log j_c \quad (4)$$

where,  $j_c$  is the cathodic current density, and  $\alpha$  is the transfer coefficient,  $j^0$  is the exchange current density.  $\eta_c$  is cathodic overpotential which calculated from the equation  $\eta_c = E - E_{eq}$ ,  $E_{eq}$  is the equilibrium potential,  $E$  is the cathodic potential). The corrosion potential ( $E_{corr}$ ) was fitted from the potentiodynamic polarization curve to be -1167 and -

1328.6 mV for concentrations 0.01 and 2.0 M respectively using the Tafel curve fitting process. This value indicates that the cathodic reactions involved a depolarization reaction to both oxygen and hydrogen.

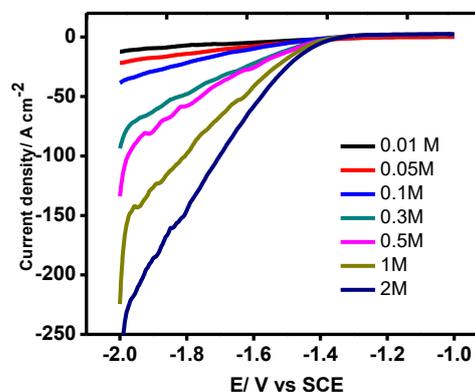


Fig. 2: Cathodic polarization curves for Fe-17Cr-14Ni alloy immersed in in stagnant naturally different concentrations of KOH solutions at 25 °C.

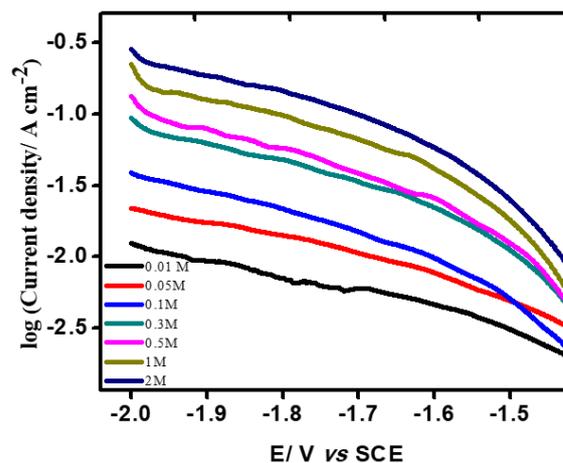
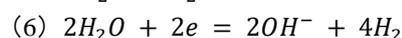


Fig. 3: Tafel plots of Fe-17Cr-14Ni alloy.

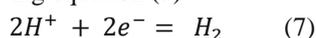
Table 1: Polarization parameters of Fe-17Cr-14Ni alloy in different concentrations of KOH at 25°C.

Conc. /M	$E_{corr}$ /mV	$\beta_c$ /mV	Corr. Rate/mpy
0.01	-1167.0	-54.8	301.8
0.1	-1340.5	-89.7	3.709
0.3	-1325.5	-89.9	5.701
0.5	-1333.8	-103.0	8.130
1	-1340.0	-101.6	10.42
2	-1328.6	-102.9	13.30

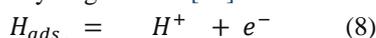
The oxygen and hydrogen depolarisation reactions are seen in Equation 5 and equation 6 respectively [19].



The hydrogen potential of the material was considered to be the most negative potential for cathodic safety. However, multiple types of researches have shown that it is not correct to characterize the potential for hydrogen evolution as the highest potential for cathodic protection since the cathode reaction is an extensive result of the oxygen and hydrogen reduction reactions [11, 16]. Tafel polarization analyses have been also carried out to understand the effect of concentration of the alkali electrolyte on the investigated commercial alloy. It may also be noted from Fig. 3 that the output of hydrogen can be regulated by adjusting the concentration of electrolytes as for the other variables within the inspection. The over-potential of the HER was calculated as the difference between the real electrode potential and the reversible potential. It is also clear from the obtained results that there is a direct relationship between the cathodic current density and the concentration of electrolytes, e.g. the cathodic current density reported in 2.0 M KOH solution at a polarization potential of -1.8 V is several times greater than that reported in 0.1 M KOH solution under the same conditions. This implies that the output of hydrogen can be regulated by the modification of the electrolyte concentration. Various pathways of reaction have been proposed to explain the mechanism of the HER in which two protons and two electrons combine to make a hydrogen molecule as the following equation (7):



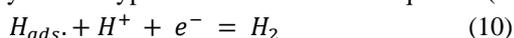
The first step of this reaction is called the Volmer reaction and given by equation (8) in which the proton and the electron react to the formation of an adsorbed hydrogen atom [20]:



The Volmer reaction is followed either by an associative reaction of two adsorbed H atoms then disorb from the electrode surface. This step is called Tafel reaction, which is a Langmuir Hinshelwood type reaction represented by equation (9) [21]:



or by the Heyrovsky mechanism, which is an EleyeReidel type reaction as shown in equation (10):



where a proton and electrons react directly on an adsorbed atomic H atom to form Hydrogen [22]. The actual direction of the reaction is not always easy to demonstrate. The calculated Tafel slope for the HER on Fe-17Cr-14Ni alloy was ranged from -55 to -103 mV (Table 1), which means that the HER obeys the

Volmer- Heyrovsky pathway. In an acid medium the situation is complicated by the corrosion of the electrode because, at the overpotential needed for oxygen evolution, the electrode material corrodes and is often passivated. In alkaline electrolytes, the situation is generally better because the electrodes can resist the corrosion. However, in this case, the formation of the metal oxide has to be taken into account.

### 3.2.2. Electrochemical impedance spectroscopic tests, EIS

The experimental impedance data of Fe-17Cr-14Ni alloy in stagnant naturally aerated different concentrations of KOH at 25°C after 15 min of electrode immersion are presented as Nyquist diagrams in Fig. 4.

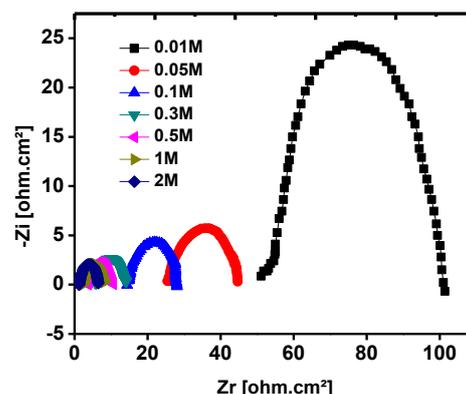


Fig.4: Nyquist plots for Fe-17Cr-14Ni alloy immersed in KOH solution of different concentrations at 25 °C.

The general behavior of Fe-17Cr-14Ni alloy shows a slight decrease in the diameter of the semicircle and also the total impedance, with the increase of the electrolyte concentration, which means a decrease in the charge transfer resistance of the electrode process. The confusing existence of the semicircles is typical of solid electrodes; such frequency dispersion has been attributed to the micro-roughness and other inhomogeneity of the solid electrode [23-26].

Fig. 5 shows the Bode plots of Fe-17Cr-14Ni alloy in stagnant naturally aerated different concentrations of KOH at 25°C after 15 min of electrode immersion. Bode plots demonstrate the presence of a single phase maximum, which means that we are concerned with a single time constant, and the mechanism of the electrode process is not influenced by the concentration of electrolytes. It has

been stated that the diameters of the high-frequency capacitive loops can be considered to be a charge transfer resistance. Software provided with the impedance system was used to analyze the impedance spectra obtained at different electrolyte concentrations, which used the depression formula for a simple equivalent model. For the presented combination the total impedance,  $Z$ , is given by the following equation :

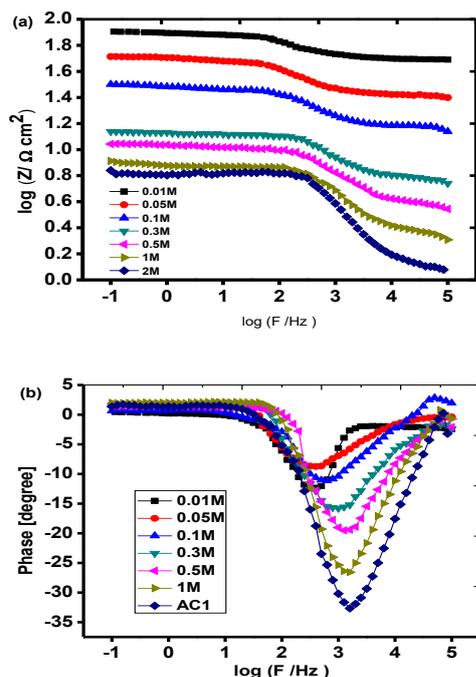


Fig.5 : Bode plots for Fe-17Cr-14Ni alloy immersed in KOH solution of different concentrations.

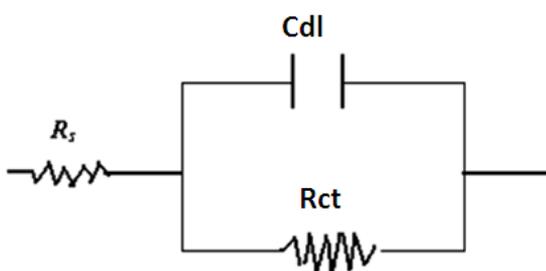


Fig. 6. The chemical equivalent circuit fitted the impedance data.

$$Z = R_s + [R_{ct} / \{1 + (2\pi f R_{ct} C_{dl})^\alpha\}] \quad (11)$$

where an empirical parameter is  $\alpha$  ( $0 \leq \alpha \leq 1$ ) and  $f$  denotes the frequency in Hz [27,28]. It is obviously indicated from the measured impedance data shown in Table 2 that, as the alkali concentration decrease as the charge transfer resistance increases marginally. It is vital to recognize that the obtained value of  $\alpha$

approaches unity in all solutions which means that the alloy/alkali interface behaves like an ideal capacitor and there is really no need to choose a constant phase element rather than the capacitor for impedance data interpretation [29].

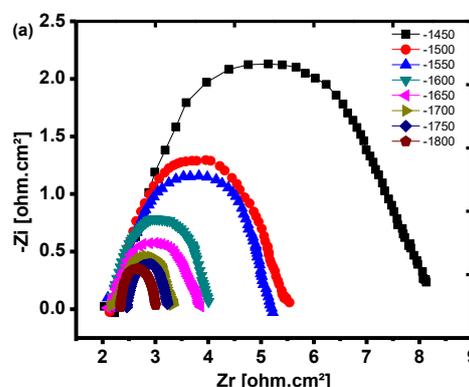
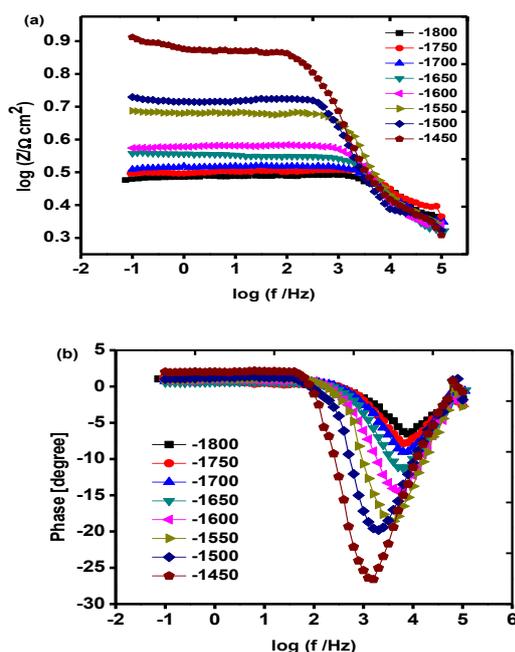


Fig. 7: Nyquist plots for Fe-17Cr-14Ni alloy immersed in 1M KOH solution at different applied cathodic potentials at 25°C.

The fitted equivalent circuit is represented in Fig. 6 and consists of the double-layer capacitance ( $C_{dl}$ ) in parallel to the charge transfer resistance ( $R_{ct}$ ), which was used previously to model the alloy/alkali interface and the literature has been described similar circuit for the tungsten as cathodic material for the evolution of hydrogen in KOH solution [23]. These findings are in agreement with the polarization data, where a lowering in charge ( $R_{ct}$ ) transfer resistance and an enhance in exchange current density are essential factors for high electrocatalytic activity towards the reaction of hydrogen evolution. At various cathodic potentials, the experimental EIS data on Fe-17Cr-14Ni alloy in stagnant naturally aerated 1M KOH was tested and recorded to investigate the effect of cathodic potentials on the rate of HER. The behavior of Nyquist and Bode plots of these measurements is shown in Fig. 7 and Fig. 8 respectively at potentials values varying from -1450 to -1800 mV. Equivalent circuit parameters obtained by fitting the experimental EIS data are recorded in Table 3. The results obtained mean that the hydrogen production can be controlled by altering the cathodic potential at a fixed electrolyte concentration, in addition to the other parameters under analysis. Based on the values of charge transfer resistance ( $R_{ct}$ ) and solution resistance ( $R_s$ ) tabulated in Table 3, it can be assumed that the corrosion rate is inversely proportional to the cathodic potential.



**Fig. 8:** Bode plots for Fe-17Cr-14Ni alloy immersed in 1M KOH solution at different applied cathodic potentials.

**Table 2:** Equivalent circuit parameters of Fe-17Cr-14Ni alloy in stagnant naturally aerated different concentrations of KOH at 25 °C.

Conc. /M	$R_s$ / $\Omega$	$R_{ct}$ / $\Omega$ cm <sup>-2</sup>	$C_{dl}$ / $\mu$ F cm <sup>-2</sup>	$\alpha_1$
0.01	50.67	50.60	12.58	0.786
0.05	25.90	19.01	26.45	0.989
0.1	14.70	13.35	29.79	0.929
0.3	5.985	7.557	33.27	0.989
0.5	3.787	6.987	28.69	0.995
1	2.324	5.887	34.06	0.992
2	1.287	5.491	45.79	0.999

**Table 3:** Equivalent circuit parameters obtained by fitting the experimental EIS recorded at various cathodic potentials on Fe-17Cr-14Ni alloy in stagnant naturally aerated 1M KOH at 25 °C.

E/ mV	$R_s$ / $\Omega$	$R_{ct}$ / $\Omega$ cm <sup>-2</sup>	$C_{dl}$ / $\mu$ F cm <sup>-2</sup>	$\alpha_1$
-1450	2.324	5.887	34.06	0.992
-1500	2.283	3.138	40.56	0.988
-1550	2.276	2.961	21.49	0.995
-1600	2.188	1.798	22.12	0.988
-1650	2.246	1.299	24.49	0.947
-1700	2.289	1.000	20.05	0.95
-1750	2.475	0.944	21.22	0.926
-1800	2.381	0.761	20.89	0.926

#### 4. Conclusions

This work has investigated the electrocatalytic properties of Fe-17Cr-14Ni electrode in 1.0M KOH for HER. Fe-17Cr-14Ni alloy can be considered as a

promising cathode for the hydrogen evolution reaction. The electrochemical behaviour of the investigated alloy, physically characterized by XRD and SEM, was studied in different concentrations of KOH solution by means of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests. The results were obtained showed that as the electrolyte concentration increased as the rate of HER increased. Polarization and impedance results on Fe-17Cr-14Ni alloy at various cathodic potential indicated that the rate of H<sub>2</sub> evolution increases with decreasing the cathodic potential. A simple electrical equivalent circuit with the double-layer capacitance ( $C_{dl}$ ) parallel to the charge transfer resistance ( $R_{ct}$ ) fitted the experimental data well. The Fe-17Cr-14Ni cathode can be operated continuously for weeks in 1.0 M KOH solution without any special treatment and the obtained rate of H<sub>2</sub> evolution on this cathode is constant all over the time of application without any cathode deterioration.

#### 5. Conflicts of interest

There are no conflicts to declare.

#### 6. Acknowledgements

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