

## Fe AND Ce EXCHANGED ZSM-5 ZEOLITES AS ELECTROCATALYSTS FOR ORR AND OER REACTIONS

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### ABSTRACT

Samples of zeolite ZSM-5, containing Ce and Fe, were tested as electro-catalysts for oxygen evolution reaction and oxygen reduction reaction, respectively, which play significant roles in energy conversion systems, such as fuel cells, rechargeable metal-air batteries and water electrolyzers. Metallic species were introduced by ion-exchange. Zeolite ZSM-5 was used in its conventional microporous form, but also in a hierarchical, mesopore-containing form, obtained by alkaline-induced demetallation. The samples were characterized by chemical analysis, low-temperature nitrogen adsorption, X-ray diffraction and diffuse reflectance UV-Vis spectroscopy. Electro-catalytic activity studies were performed by cyclic/linear sweep voltammetry in alkaline media. Among the investigated samples, the hierarchical ZSM-5 exchanged with Fe was shown to possess the best properties/performance, for both oxygen evolution and oxygen reduction reaction. In the case of oxygen reduction, the hierarchical sample exhibited the highest onset potential, while in the oxygen evolution reaction, its use resulted in the highest current density, as well as the lowest onset potential. No direct correlation between electro-catalytic activity and the amount of the metallic species in the zeolites were found. The superior behavior of the hierarchical sample could be related to the high degree of dispersity of iron species, as it was detected by diffuse reflectance UV-Vis spectroscopy.

Key words: bifunctional electro-catalysts, oxygen evolution reaction, oxygen reduction reaction, ion-exchanged zeolites.

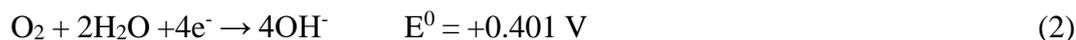
### INTRODUCTION

Due to many adverse environmental issues, related to the use of fossil fuels, there is an urgent need for efficient “green” energy conversion systems. In the domain of electrochemical conversion pathways, several systems, most notably water electrolyzers, fuel cells and metal-air batteries have been extensively studied [1]. A series of electrochemical reactions lie at the core of these systems, including oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Both reactions demand a suitable catalyst and can be performed in alkaline or acidic media, with alkaline electrolytes being regarded as more favourable [2].

The OER reaction in alkaline conditions can be summarized as:



The ORR reaction can proceed via a “direct” reaction:



or a multistep pathway:



Typically, noble metal-based catalysts are the most efficient for ORR and OER. However, due to the inherent differences of the reactions themselves, especially different electric potentials, only a small number of them have been proven to be applicable for both reactions. Hence, formulating highly active and durable electro-catalysts, notably bifunctional ones, is still a challenge. Among various materials, zeolite-based catalysts have been probed with some success [3,4]. In this paper, the applicability of Ce and Fe exchanged zeolite ZSM-5 for OER and ORR is considered, including the influence of the porosity alteration.

## **EXPERIMENTAL**

Starting from zeolite ZSM-5 (Zeolyst;  $[\text{SiO}_2/\text{Al}_2\text{O}_3] = 23$ ), ion-exchanged samples were prepared by ion exchange, at room temperature Cerium was introduced using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich, 0.003 M, 5g zeolite/L) and iron using  $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  (Sigma, 0.01 M, 3g/50 mL). The mixtures were stirred for 7 days and subsequently washed with deionized water, dried at 120 °C and calcined in air at 500 °C for 5h. For ion exchange with Fe, a hierarchical form of the starting zeolite was also used. The hierarchical ZSM-5 was prepared prior to ion-exchange, using demetallation with NaOH (0.2 M, 90 °C, 30 min), followed by an acid wash (0,1 M HCl, 25 °C, 6 h). The obtained samples were labelled as Ce-ZSM-5, Fe-ZSM-5 and Fe-ZSM-5H (hierarchical sample). All samples were characterized using low temperature  $\text{N}_2$  adsorption (Micromeritics 2010, pre-treatment at 400 °C, 4 hours), X ray diffraction (Rigaku Ultima IV diffractometer. Cu  $K\alpha$  radiation,  $\lambda=1.54178 \text{ \AA}$ , from 4° to 50° 2 $\theta$ , 0.020° step, 1°/min), diffuse reflectance UV-Vis spectroscopy (Agilent Cary 5000 UV-Vis-NIR) and elemental chemical analysis.

Catalytic inks were prepared by ultrasonically dispersing 5 mg of the corresponding electro-catalyst and 0.6 mg Vulcan XC72R in 40  $\mu\text{L}$  of 2 wt. % polyvinylidene difluoride solution in N-methyl 2-pyrrolidone, for 30 min. The working electrodes were prepared by pipetting 10  $\mu\text{L}$  of each catalytic ink onto glassy carbon (GC) supports and leaving it to dry at room temperature. Current densities were calculated using the geometric area of GC supports. All electrochemical measurements were done using Ivium Potentiostat/Galvanostat in a one-compartment glass cell of 40 mL volume with Pt foil and saturated calomel electrode (SCE), serving as counter and reference electrodes, respectively. All potentials within this paper are given relative to the reversible hydrogen electrode (RHE) reference. For ORR studies, the cyclic voltammograms (CV) were recorded in 1 M KOH (analytical reagent grade, Fisher Chemicals) solution saturated with  $\text{O}_2$  (>99.999%, Messer), scanning the potential from 1.1 to 0.3 V at scan rate of 20 mV/s. Linear sweep voltammograms (LSV) with RDE were recorded at scan rate of 5 mV/s and rotation rates ranging from 200 to 1800 rpm set by Pine AFCPRB rotator. For OER studies, LSVs were run in 1 M KOH electrolyte solution from the open circuit potential (OCP) up to 2 V at scan rate of 5 mV/s.

## **RESULTS AND DISCUSSION**

ORR at different samples was systematically studied in  $\text{O}_2$ -saturated 1 M KOH. Control CVs of all three materials, recorded in deaerated 1 M KOH solutions, showed only small redox peaks corresponding to Ce or Fe reduction (not shown). However, upon saturation of the solution with  $\text{O}_2$ , a notable increase of current density could be seen, with the appearance of a well-defined peak corresponding to the oxygen reduction (Figure 1A).

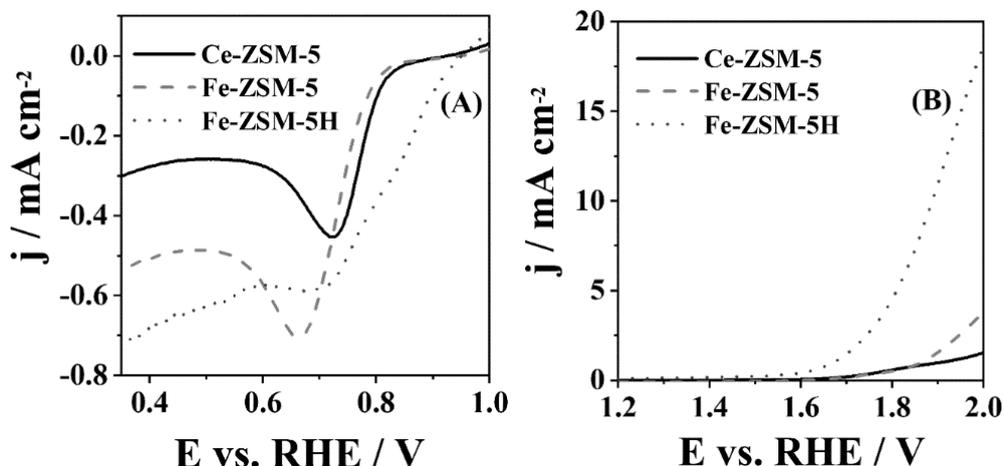


Figure 1. Voltammetric responses of three studied zeolites under ORR (A) and OER (B) polarization conditions.

One of the key parameters for evaluating the performance of ORR catalysts is the onset potential (the more positive onset potential, the better the activity for the ORR). CV of the Fe-ZSM-5H in O<sub>2</sub>-saturated 1 M KOH solution showed the ORR onset potential of 0.93 V. ORR onset potentials in case of Ce-ZSM-5 and Fe-ZSM-5 were found to be similar and less positive (Figure 1A, Table 1). In the case of OER (Figure 1B), lower values of the onset potential are favourable. Among the investigated samples, the lowest onset potential (defined as the potential to reach the current density of 1 mA/cm<sup>2</sup>) was detected in case of Fe-ZSM-5H, indicating its highest activity. This was further confirmed by the highest current density at the overpotential of 400 mV recorded using this sample.

Table 1. Comparison of parameters for evaluating the performance of ORR and OER catalysts.

	Ce-ZSM-5	Fe-ZSM-5	Fe-ZSM-5H
<b>ORR</b>			
E <sub>onset</sub> (V)	0.83	0.82	0.93
E <sub>p</sub> (V)	0.72	0.66	0.68
j <sub>p</sub> (mA/cm <sup>2</sup> )	-0.46	-0.71	-0.59
<b>OER</b>			
E <sub>onset</sub> (V)	1.86	1.86	1.74
j <sub>400</sub> (mA/cm <sup>2</sup> )	0.06	0.06	0.67

It is interesting that the electro-catalytic results did not necessarily correlate with the amounts of Ce or Fe present in the samples (1.0 % Ce, 0.26 % Fe in Fe-ZSM-5 and 0.35 % Fe in FeZSM-5H). Rather, the superior performance of the hierarchical sample Fe-ZSM-5H could be attributed to the high dispersity of Fe species in the zeolite, which was evidenced by DR UV-Vis spectra (Figure 2). The spectra of the conventional microporous Fe-ZSM-5 revealed the presence of a large amount of Fe oxide species (> 400 nm), which could lower the amount of actually active Fe species. On the other hand, in Fe-ZSM-5H mostly isolated Fe ions (< 300 nm) and small oligoclusters (300 - 400 nm) were detected [5]. The difference in Fe dispersity in Fe-ZSM-5 and Fe-ZSM-5H can be related to the existence of mesopores in the hierarchical sample (pore size distribution not shown here), and the related increase of mesoporous/external surface ( $\approx 80 \text{ m}^2$ ), measured by nitrogen adsorption.

To further investigate the electro-catalytic activity of Fe exchanged zeolites, OER reaction was conducted in the presence of H<sub>2</sub>O<sub>2</sub> [6]. The addition of peroxide (results not shown here) significantly enhanced the activities of both samples; the superior behaviour of the hierarchical sample was even more pronounced, in terms of both onset potential and current density.

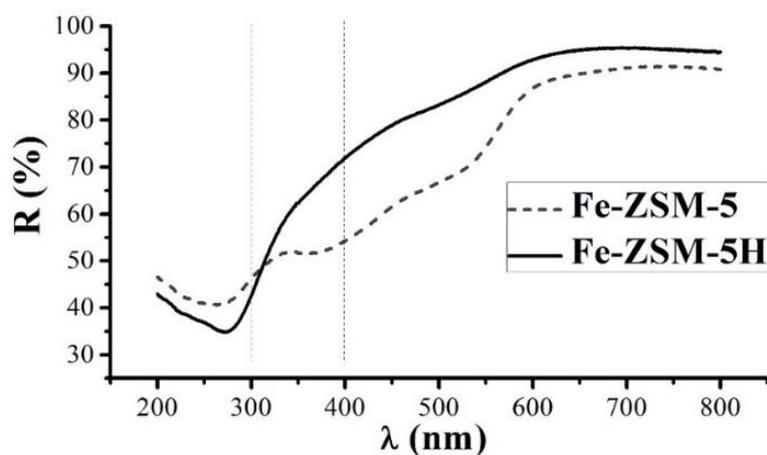


Figure 2. DR UV-Vis spectra of Fe-ZSM-5 and Fe-ZSM-5H.

## CONCLUSION

Transition metal-exchanged ZSM-5 zeolite samples were successfully applied as electrocatalysts for oxygen evolution and oxygen reduction reactions. Although the presented results can only be considered as preliminary, they clearly show that the modifications of the zeolitic porous structures prior to ion exchange can significantly improve their electrochemical performance. The overall highest activity, as judged by the values of onset potentials and current densities, was measured for the hierarchical Fe-ZSM-5H sample. It is very probable that its favourable properties were due to the induced mesoporosity, which altered the form of the introduced iron species. Hence, in order to further improve zeolite-based electrocatalysts for ORR and OER, special attention should be paid to the nature of metallic species in the zeolitic framework (isolated ions, small oxide clusters, large oxide particles) and the related porosity variations of the starting zeolitic materials.

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