

# Encapsulation of Pt-based mono- and bimetallic Carbonyl Clusters into ZIF-8 for Electrocatalytic Applications

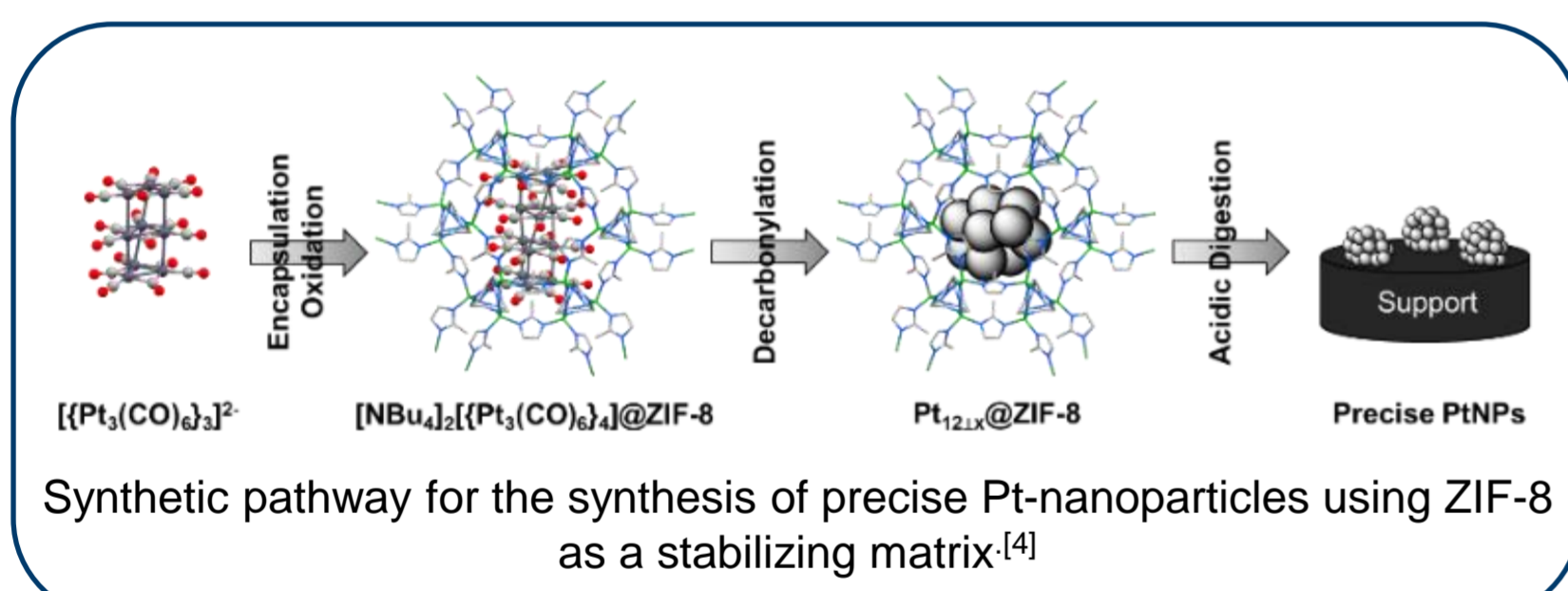
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## Introduction

The oxygen reduction reaction (ORR) occurring in fuel cells is currently catalysed by platinum, the best known catalyst regarding activity and stability.<sup>[1]</sup> Problematic hereby are the high costs of Pt-catalysts<sup>[2]</sup>, which ask for the search of similar active alternative catalysts with lower platinum amount. This can be achieved by either nanostructuring or alloying the Pt-catalysts with non platinum group metals (PGM).<sup>[3]</sup> Nanostructuring leading to monodisperse nanoparticles depicts a huge synthetic challenge since agglomeration processes have to be suppressed. One way to meet this challenge is to encapsulate the Pt-cluster precursors into metal-organic-frameworks (MOFs) during the synthesis.<sup>[4]</sup> The aim of this work was the encapsulation into the zeolitic imidazolate framework ZIF-8 [Zn(2-MeIM)] and activation of seven mono- and bimetallic Pt-clusters synthesised by the ZACCHINI group, as well as the electrochemical testing of one of the obtained encapsulated bimetallic Pt-cluster. The seven clusters are the following:  $(PPh_4)_4[Pt_6(SnCl_2)_2(SnCl_3)_4(CO)_6]$ ,  $(NEt_4)_2[Pt_5Ni(CO)_{12}]$ ,  $(NEt_4)_4[Pt_{16}Ni_3(CO)_{22}]$ ,  $(NBu_4)_4[Pt_6Ni_6(CO)_{22}]$ ,  $(NBu_4)_4[Pt_{27}(CO)_{31}]$ ,  $(NEt_4)_2[Fe_3Pt_3(CO)_{15}]$ ,  $(NEt_4)_2[Fe_4Pt_6(CO)_{22}]$  (the clusters will be denoted as  $Pt_6Sn_6$ ,  $Pt_5Ni$ ,  $Pt_{16}Ni_3$ ,  $Pt_6Ni_6$ ,  $Fe_3Pt_3$ ,  $Fe_4Pt_6$ ,  $Pt_{27}$  in the following).<sup>[5-7]</sup> The encapsulation of the clusters was analysed via Powder X-Ray Diffraction (PXRD), Infrared Spectroscopy (IR) and Elemental Analysis (EA). Electrochemical testing was performed on one of the encapsulated and activated bimetallic Pt-based Carbonyl Cluster using Rotating Disk Electrode (RDE).

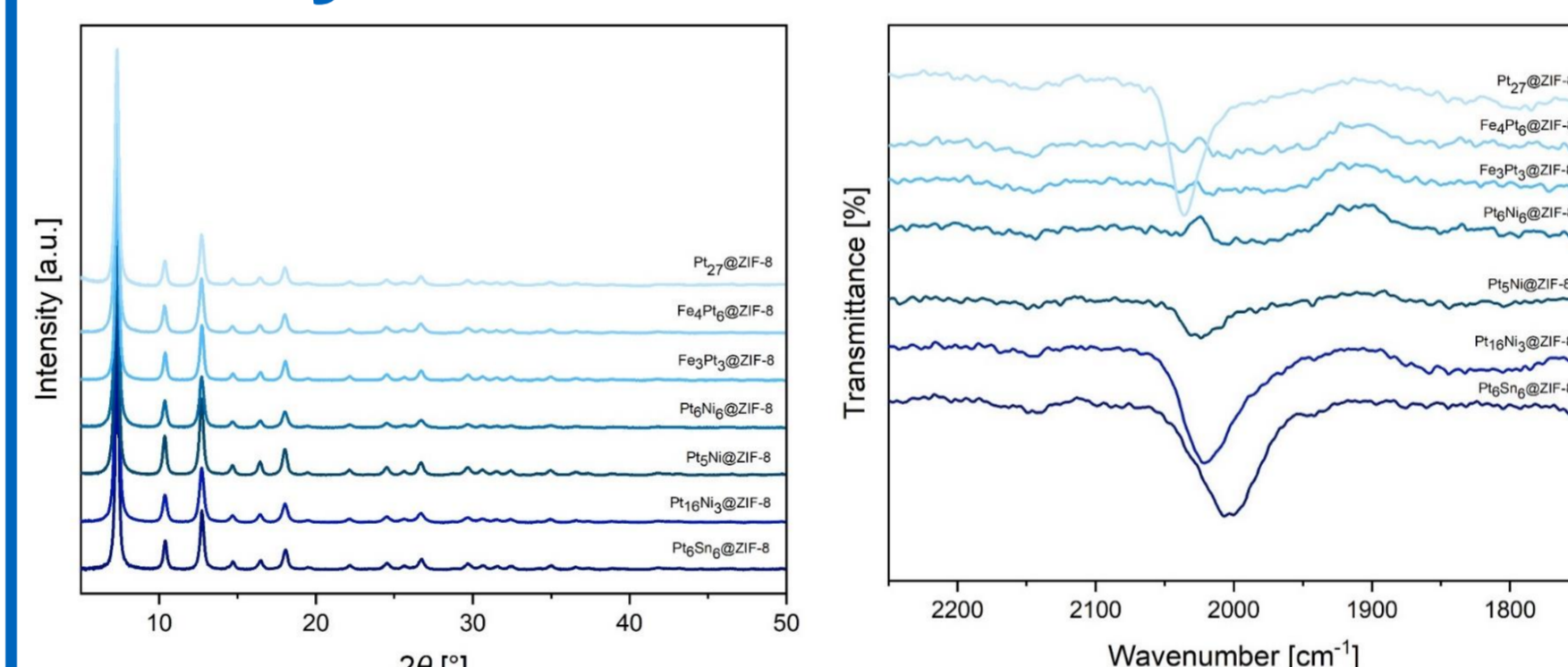
## Synthesis Pathway

In a work by Kratzl *et al.* the synthesis of precise Pt-nanoparticles starting from the precursor Pt-cluster  $[Pt_3(CO)_6]^{2-}$  using ZIF-8 as stabilizing matrix was described.<sup>[4]</sup> For the encapsulation and activation of the seven clusters in this work the same pathway was used.



The encapsulation occurred by the *in-situ* formation of ZIF-8 by adding a MeCN solution of 2-Methylimidazolate (2-MeIM) to a MeCN solution of  $Zn(NO_3)_2$ , whilst a MeCN solution of the cluster was added simultaneously. In the next step the samples were activated by removing the carbonyl ligands of the clusters by heating the samples at 200 °C under vacuo for 2 h. For electrochemical testing one of the encapsulated clusters was supported on *Vulcan*® by acidic digestion of the MOF.

## Analysis



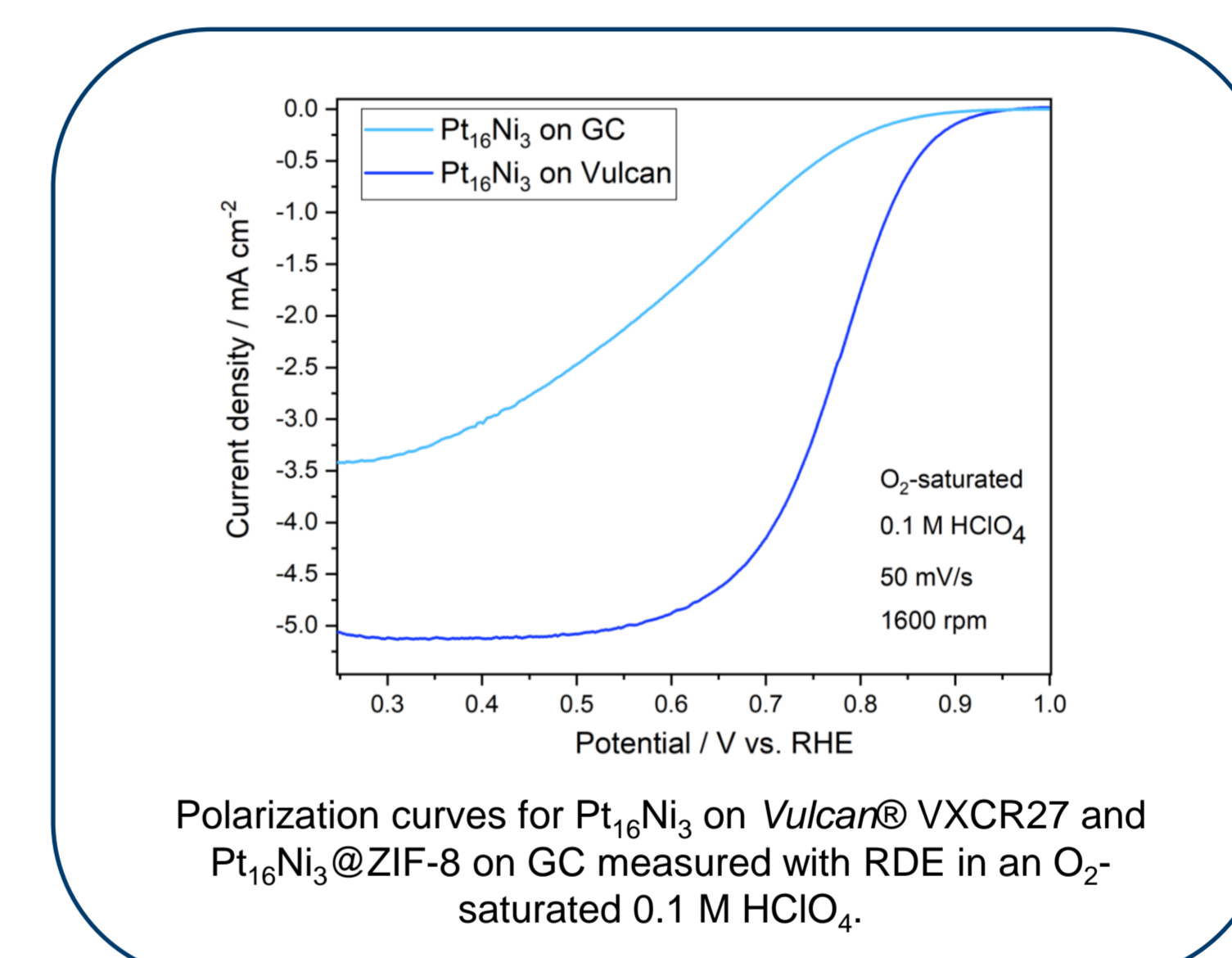
Diffraction patterns displaying the characteristic pattern for crystalline ZIF-8<sup>[4]</sup> (left) as well as IR spectra displaying the region of carbonyl bands (right) for all seven samples after encapsulation.

The formation of ZIF-8 was confirmed by obtained diffraction patterns, displaying the characteristic pattern for crystalline ZIF-8.<sup>[4]</sup> The encapsulation of the clusters was indicated by IR spectra, displaying partially signals for the CO ligands of the clusters. Further the amount of encapsulated cluster was determined by EA.

EA results for the metals of all seven encapsulated clusters.

Cluster	Measured wt%	Calculated wt%
$Pt_6Sn_6$	Pt: 1.92, Sn: 0.90	Pt: 3.07, Sn: 1.87
$Pt_{16}Ni_3$	Pt: 3.60, Ni: 0.10	Pt: 7.59, Ni: 0.48
$Pt_5Ni$	Pt: 1.00, Ni: 0.02	Pt: 3.59, Ni: 0.22
$Pt_6Ni_6$	Pt: 0.70, Ni: <0.30	Pt: 3.49, Ni: 1.05
$Fe_3Pt_3$	Pt: <0.03, Fe: 0.04	Pt: 3.87, Fe: 1.11
$Fe_4Pt_6$	Pt: <0.03, Fe: 0.02	Pt: 4.74, Fe: 0.90
$Pt_{27}$	Pt: 2.10	Pt: 6.17

## Electrochemical Testing



Of the seven clusters the  $Pt_{16}Ni_3$ -cluster was tested electrochemically on glassy carbon (GC) as well as on *Vulcan*® with RDE. Both clusters displayed an activity in the ORR, but the activity of the cluster supported on *Vulcan*® was higher than the activity of the cluster on GC. Assuming the theoretical amount of Pt in the used 2 mg of the sample, the cluster on GC showed a mass activity of 3.22  $mA/mg_{Pt}$  and on *Vulcan*® a mass activity of 58.4  $mA/mg_{Pt}$ , displaying lower mass activities than known Pt-Ni alloy catalysts.<sup>[8]</sup>

## Conclusion

It could be shown that the encapsulation of the mono- and bimetallic clusters into ZIF-8 was successful, however for some of them higher amounts of the cluster could be encapsulated, whereas for others only small amounts could be encapsulated. Especially low amounts of the  $Fe_3Pt_3$ - and  $Fe_4Pt_6$ -cluster could be encapsulated successfully into ZIF-8. But even for the clusters, which could be encapsulated in higher amounts not the full amount of Pt-cluster given to the reaction mixture could be encapsulated, mostly only less than half of it. The successful encapsulation could be confirmed by PXRD, IR and EA measurements. The electrochemical testing of the  $Pt_{16}Ni_3$ -cluster on GC as well as *Vulcan*® displayed different mass activities, but lower mass activities than the mass activities of known Pt-Ni-alloy catalysts.

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