

# Manufacture of Platinum Nickel Co-Catalysts for HT-PEM Fuel Cells

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## Introduction

High temperature proton exchange membrane fuel cells (HT-PEM) emerged to be a promising technology for stationary applications. Positive characteristics, such as efficient fuel conversion and high energy density, led to their first niche commercialization in recent years. Due to their elevated operating temperatures of about 160 °C, enhanced reaction kinetics on both electrodes, a higher CO tolerance and an easier product water management can be achieved [1]. However, the oxygen reduction reaction (ORR) on the cathodic side is still the rate determining step and is responsible for significant overpotential losses. As expensive and scarce platinum is used as the catalyst for this reaction, alloying platinum with first-row transition metals such as nickel, is a promising way to reduce the platinum loading and hence manufacturing costs [2].

## Manufacture of PtNi/C Co-Catalysts

A previously established, straightforward and scalable synthesis procedure for PtCo/C co-catalysts was adapted and optimized for the manufacture of PtNi/C co-catalysts. First, an impregnation solution was prepared, which consisted of  $H_2PtCl_6 \cdot 6H_2O$  and  $Ni(NO_3)_2 \cdot 6H_2O$  as metal precursors dissolved in iso-propanol and ultrapure water, ethylene glycol as reducing agent and a surfactant. Pre-prepared gas diffusion electrodes (GDE) with high surface area carbon were then impregnated with this solution (platinum loading =  $1.00 \text{ mg cm}^{-2}$ ) and the precursor salts reduced at 290 °C for 10 min in  $N_2$ -atmosphere (Fig.1).

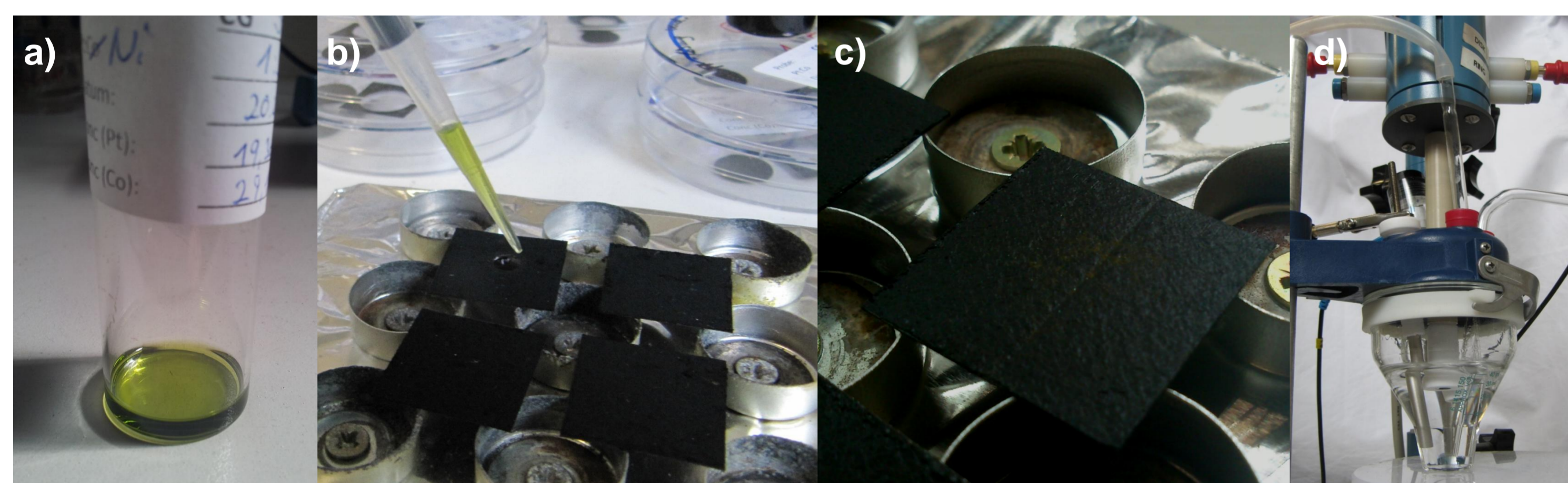


Fig.1: Impregnation of the GDE with the green precursor solution (a,b), the GDE after the reduction process (c) and the CV set-up for ex-situ characterization (d).

In order to prepare the sample for ex-situ characterization, a 2  $\text{cm}^2$  disk of the impregnated GDE pad was suspended in iso-propanol in an ultrasonic bath. A part of this homogeneous dispersion was pipetted onto a glassy carbon disk, resulting in a platinum loading of  $28 \mu\text{g cm}^{-2}$ . A similarly manufactured Pt/C-standard, with a platinum loading of  $1.20 \text{ mg cm}^{-2}$  on the GDE, was prepared the same way.

## Characterization

Electrochemical characterization was carried out by means of cyclic voltammetry (CV) with a rotating disc electrode (1600 rpm) using a Metrohm Autolab (Type PGSTAT302N) potentiostat. As electrolyte 0.1 M  $HClO_4$  in ultrapure water was used and flushed either with  $N_2$  or  $O_2$ . The electrochemical active surface area (ECSA), as well as the specific current density and the mass activity were evaluated [3].

To measure the stability of the catalyst an accelerated stress test (AST) was defined, subjecting the catalyst to three times 555 cycles from 0.5 V to 1.4 V vs. RHE (rate  $0.5 \text{ V s}^{-1}$ ). Then the ECSA loss in percent was determined.

## Results and Conclusion

Although no increase of the PtNi/C co-catalyst's ECSA compared to the Pt-standard can be seen (Fig.2b), the co-catalyst shows a higher activity towards the ORR (Fig.2a) and a higher kinetic current density (see tafel plot Fig.2c).

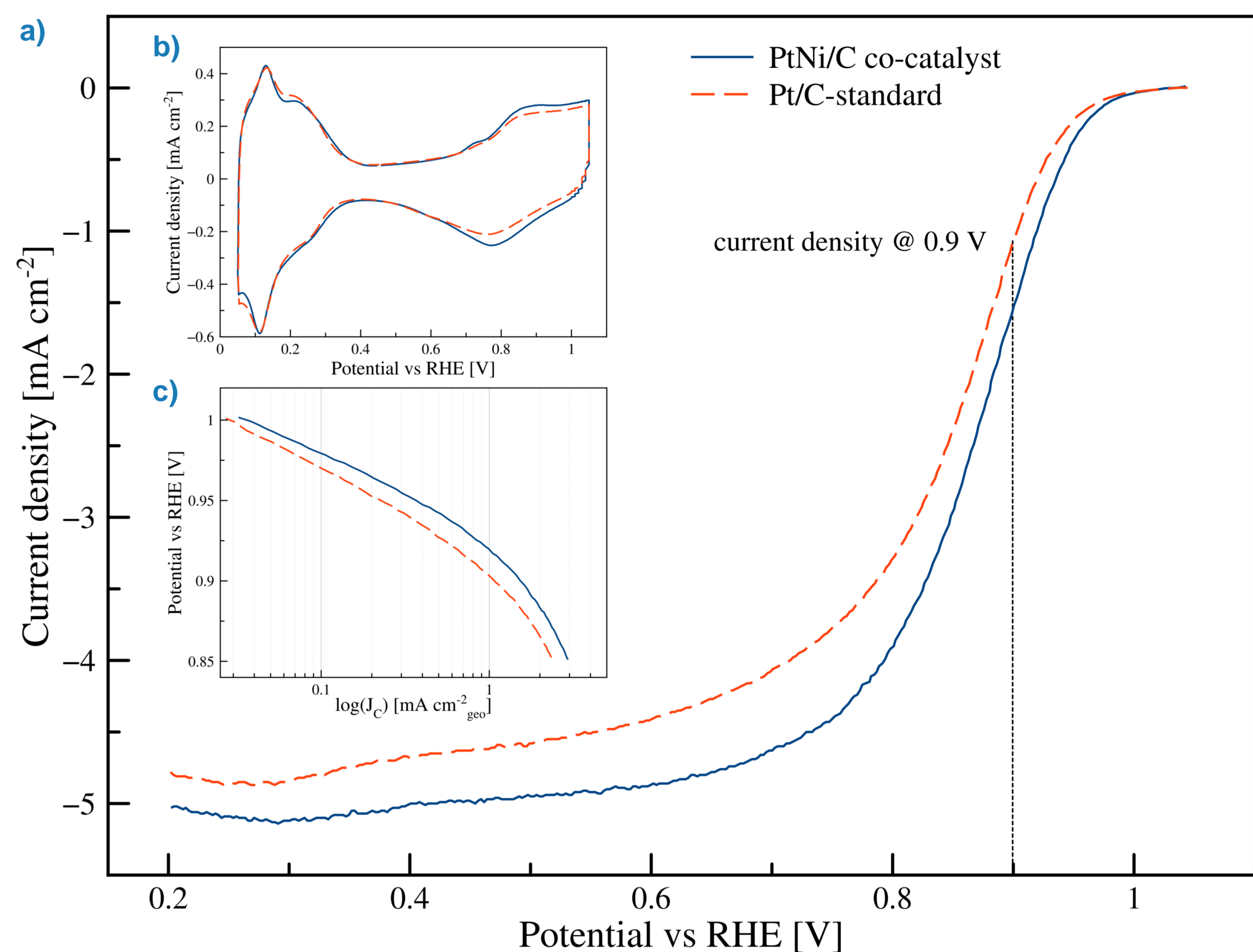


Fig.2: Comparison of PtNi/C co-catalyst to a Pt/C standard: observation of the ORR (a), CVs for ECSA evaluation (b) and tafel plot (c) in 0.1 M  $HClO_4$

The specific current density as well as the mass activity were increased significantly, while decreasing the platinum loading by 20%. An increase in the catalyst's stability compared to Pt/C could be achieved (Tab.1). Further stabilization steps such as leaching, which raised the stability of PtCo/C co-catalysts, had no effect on the PtNi/C catalyst.

Tab.1: Comparison of the results of the CV measurements

|  | Pt/C standard | PtNi/C co-catalyst |
|--|---------------|--------------------|
| Initial ECSA [ $\text{cm}^2 \text{ mg}^{-1}$ ]   | 260           | 261                |
| Degradation after 1 <sup>st</sup> AST cycle      | 29%           | 21%                |
| Degradation after 2 <sup>nd</sup> AST cycle      | 42%           | 27%                |
| Degradation after 3 <sup>rd</sup> AST cycle      | 49%           | 39%                |
| Specific current density [ $\text{mA cm}^{-2}$ ] | 0.188         | 0.295              |
| Mass activity [ $\text{A mg}^{-1} \text{ Pt}$ ]  | 0.049         | 0.077              |

Through optimization of the manufacturing process, e.g. varying the composition of the impregnation solution, reduction time and temperatures, an improved ORR co-catalyst containing nickel could be synthesized.

## Acknowledgement

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