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Synthesis dependent composition and electrocatalytic properties of Pt_xCo_{1-x} alloys

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Abstract

Pt based alloys are a matter of considerable interest as catalysts for polymer electrolyte fuel cells (PEMFC) because of their very high activity for the oxygen reduction reaction (ORR). In this work we present a systematic study on different impregnating and colloidal methods for preparing very well distributed and highly active Pt_xCo_{1-x} alloys supported on a commercial carbon black support (E-Tek/Ketjen black). Additionally to promote the alloying effect, the samples were heat treated in a reducing atmosphere. Finally, to study the influence of the different methods and the heat treatment on the alloy particle size and metal composition, Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDX) and Inductive Coupled Plasma Spectroscopy (ICP) were conducted.

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Motivation & objectives

- Synthesis of very active PtCo alloy NPs with narrow size distribution
- Study the influence of synthesis method on activity, particle size and stoichiometry
- Study the influence of heat treatment (300-800 °C) on activity and particle size
- Comparison of the different synthesis methods used
- Investigate the stability of the catalysts after prolonged electrochemical dealloying

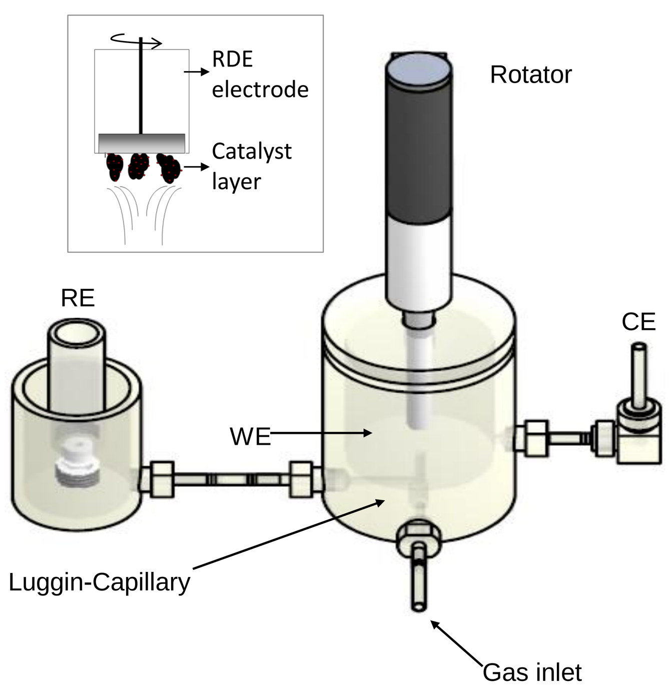


Fig. 1 Rotating Disc Electrode (RDE) setup used for the electrochemical characterization. Inset, catalyst layer.

Results & Discussion

Catalyst characterization

- Electrochemical
  - Specific activity (ORR)
  - ECSA
- TEM
  - EDS vs ICP

Catalyst	Pt:Co ratio	ECSA (m^2/g_{Pt})	Specific activity (mA/cm^2)	Square waves (0.6-1.0V) 7000 cycles (18hours) Surface area loss (%)
Impregnation method A	86:14	53	1.1	N/A
Impregnation method A Heat treatment (500 °C)	87:13	46	1.15	N/A
Impregnation method A Heat treatment (800 °C	90:10	26	1.3	N/A
Impregnation method B	55:45	68	1.15	33
Impregnation method B Heat treatment (500 °C)	60:40	62	1.5	N/A
Colloidal method A	Traces of Co	60	0.79	N/A
Colloidal method B	Traces of Co	62	0.81	40
Combination method	92:8	59	0.85	17
Pt/C	100	58	0,45	45

Table 1. PtCo alloy properties comparison

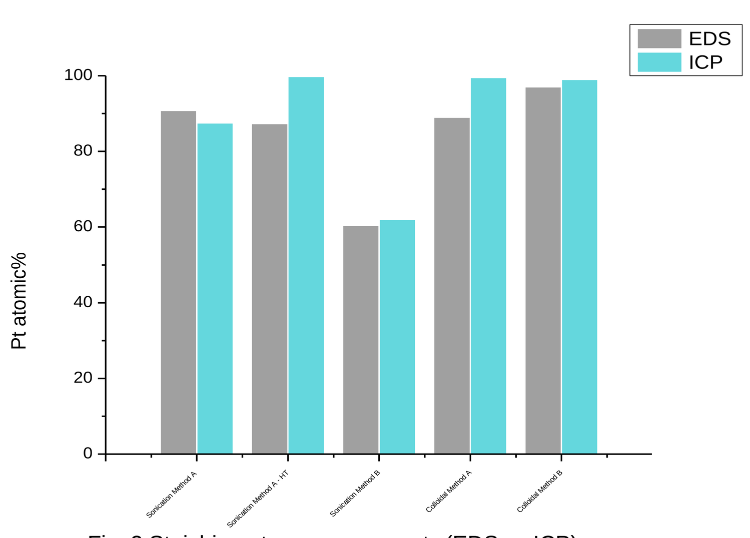
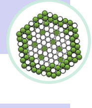


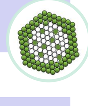
Fig. 2 Stoichiometry measurements (EDS vs ICP)

- Heat treatment
  - Specific activity enhancement
  - Particle size growth and Platinum segregation

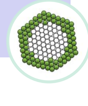
Pt and Co mapping w/o heat treatment



Pt and Co mapping with 500C heat treatment



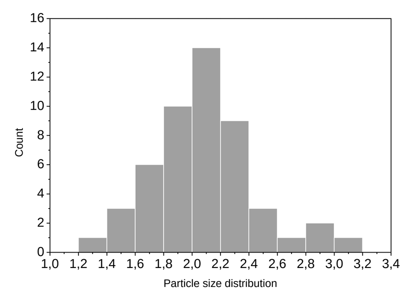
Pt and Co mapping with 800C heat treatment



Catalysts comparison

Colloidal methods

- Different polyols and metal precursors
- Very easy control of catalyst loading on the support
- Unsupported PtCo alloy nanoparticles
- - Narrow size distribution (~2nm).
  - Very good distribution on the support



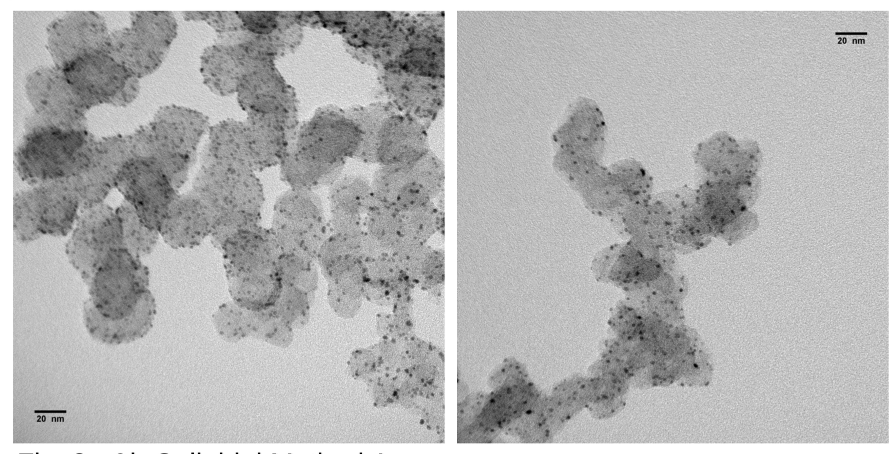


Fig. 3 a&b Colloidal Method A

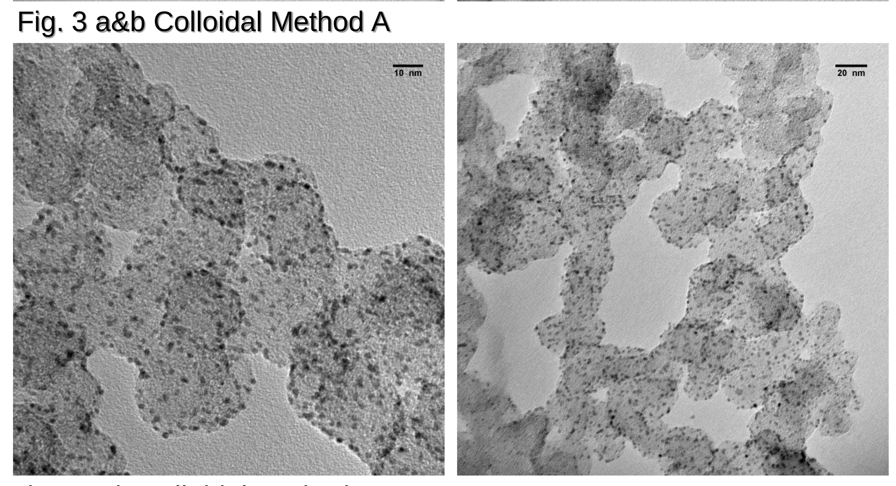
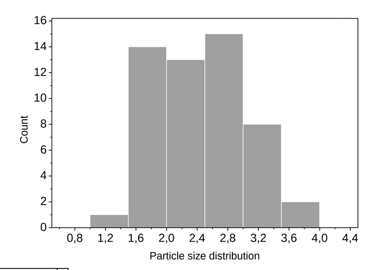
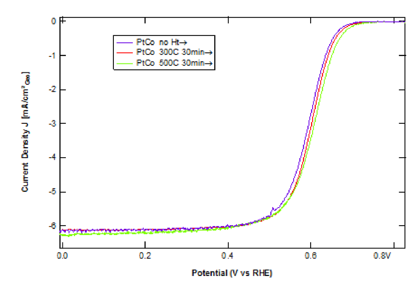


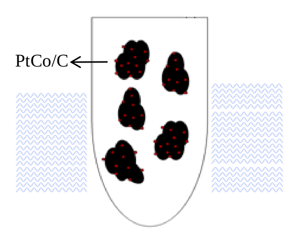
Fig. 4a&b Colloidal Method B

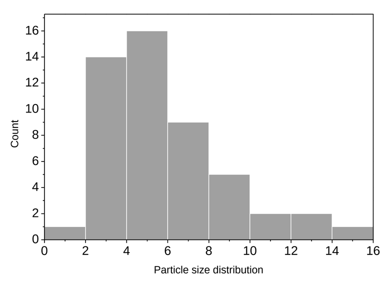
Sonication/Impregnation methods

- - Growth of PtCo alloy on EC300 support
- - Difficult size and distribution control
  - Particle size (~2,6nm)
  - After heat treatment (~5,3nm)
- Sonication during the impregnation process enhances the alloying and the particle distribution on the support









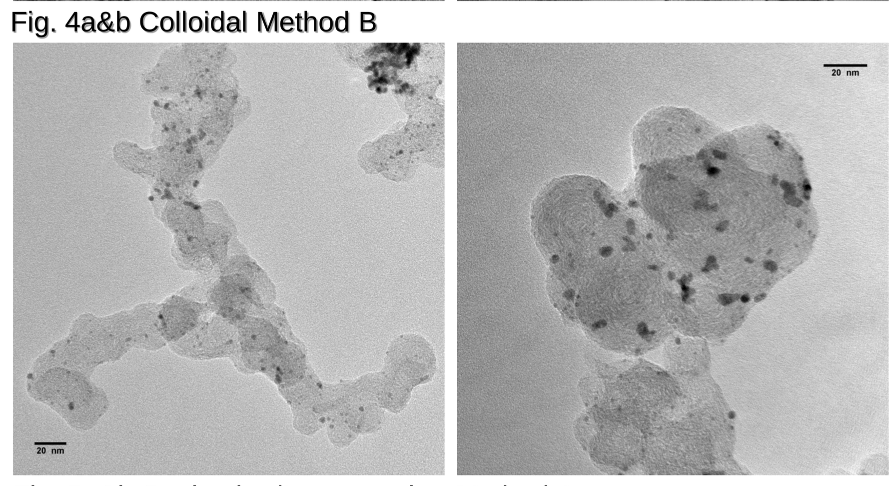


Fig. 5a&b Sonication/Impregnation Method A

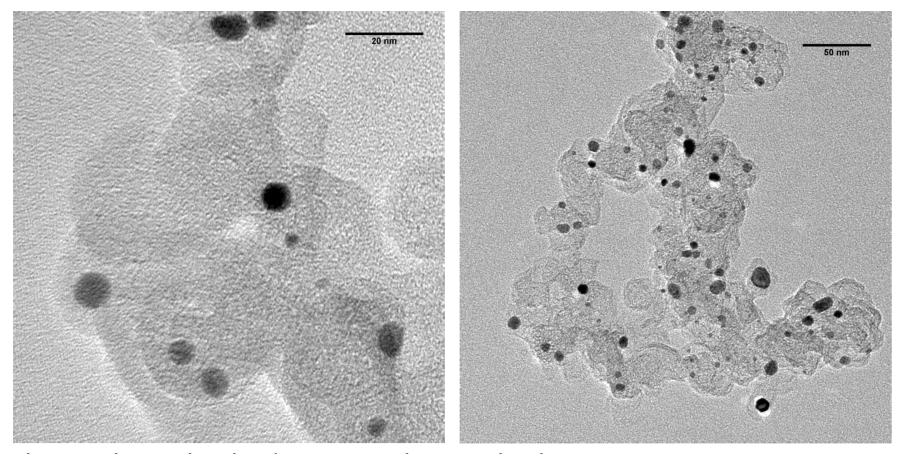


Fig. 6a&b Sonication/Impregnation Method A - Heat Treatment

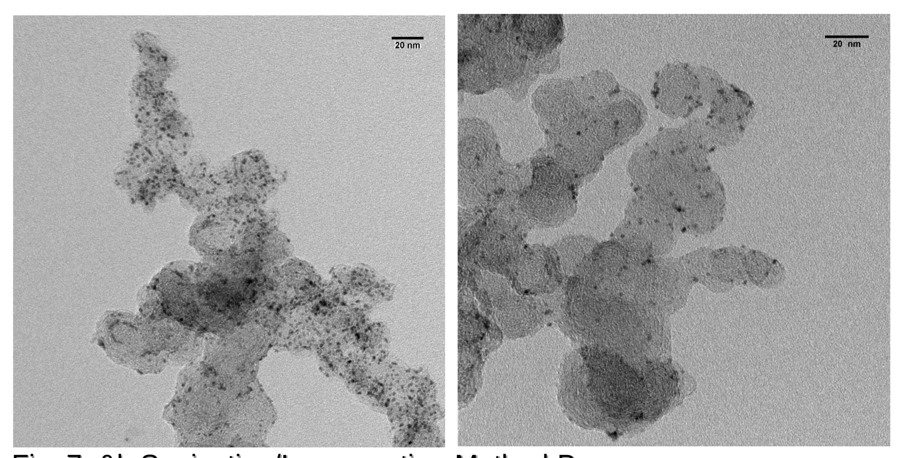
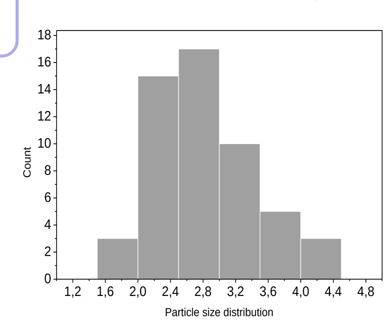


Fig. 7a&b Sonication/Impregnation Method B

Combination method

- Combination of Chemical and Colloidal methods (Pt/C colloidal sample used as seeds)
- -Easy size control. Particle size (~2,8nm)
  - Good activity
- Advantages of both methods
- Core-shell structures



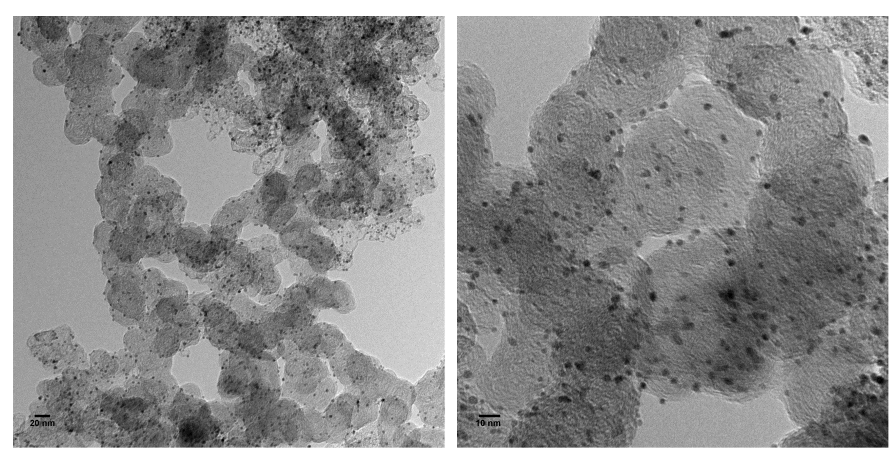


Fig. 8a&bCombinatorial Method

Outlook

Comparison of synthesis methods

- Colloidal methods
  - Very good particle distribution on the support
  - Higher activity than Pt colloidal catalyst
  - Active catalysts but lower stability
- Sonication Impregnation methods
  - Higher activity than PtCo colloidal catalysts
  - Not very good distribution on the support
  - Very active catalysts with good stability
- Combination method
  - Higher activity than colloidal samples
  - Very good distribution on the support
  - Active catalysts with very good stability

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