Surface characterization

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Performance of vertically oriented graphene supported platinum-ruthenium bimetallic catalyst for methanol oxidation

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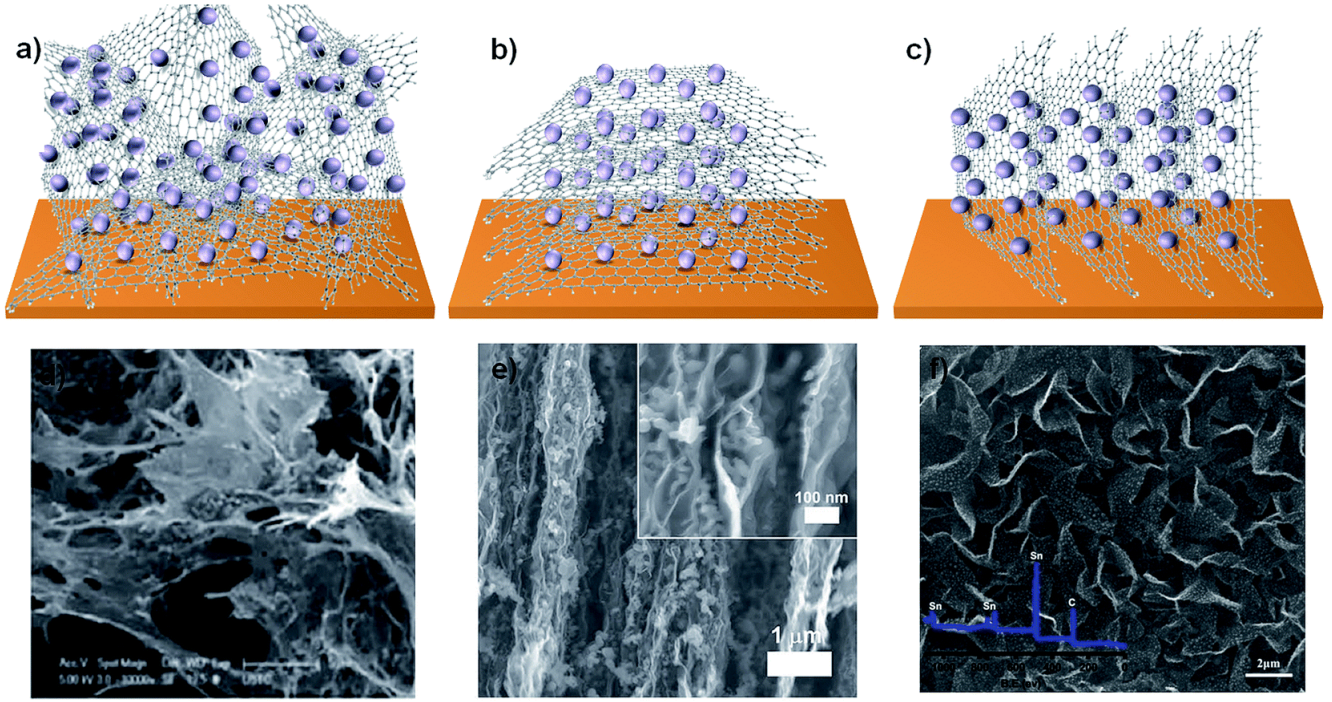
By Barbora Pijáková

Aim of the work

- Preparation of catalyts for methanol fuel cells
- Vertically oriented graphene substrate covered by Pt-Ru nanoparticles acting as catalyst for methanol oxidation reaction
- Comparison of electrocatalytic performance (mass loading; size of nanoparticles; catalytic stability) of Pt-Ru/VG products with the Pt-Ru/CP



Preparation of Pt-Ru/VG catalyst

- Substrate CP

  1. VG grown via PECVD

- Microwave source
- 5 min pretreatment, 350 W, 50 sccm of hydrogen
- 2 min deposition, 50 V bias, 50 sccm of hydrogen + 10 sccm of methane

  2. Co-electrodeposition of Pt-Ru

- Electrolyte: $H_2PtCl_6.6H_2O$ (1-9 mM)+$RuCl_3.xH_2O$ (9-1 mM)+H_2SO_4 (0.5 M)
- Three-electrode system (Pt foil = counter electrode; saturated calomel electrode = reference electrode; substrate = working electrode)
- Pulse potentials approach; 300 cycles; -0.40 V for 100 ms (deposition); 0.60V for 300 ms (diffusion of metal cations in electrolyte)

Characterization

1. Electrochemical measurement

- Cyclic voltammetry – catalytic activity
- Chronoamperometry – stability of catalyst

2. Material characterization

- Scanning electron microscopy – surface morphology; size and dispersion of Pt-Ru particles
- High resolution transmission electron microscopy
- X-ray diffraction – crystalline structures of Pt, Ru
- X-ray photoelectron spectroscopy – chemical states of Pt and Ru
- Inductively coupled plasma mass spectrometry – catalyst loading mass on substrate

Used instrumentation

- SEM: SU-70 scanning electronic microscopy (SEM, Hitachi)
- TEM: Tecnai G2 F30 STwin transmission electron microscopy (TEM, Philips-FEI)
- XRD: XRD-6000 Diffractometer with Cu Kα source (λ = 0.15425 nm, Shimadzu)
- XPS: VG Escalab Mark II with a monochromatic Mg Ka X-ray source (1253.6 eV, West Sussex)
- ICP: XSENIES, Thermo Electron Corporation

Scanning electron microscopy (SEM)
High resolution transmission electron microscopy (HRTEM)

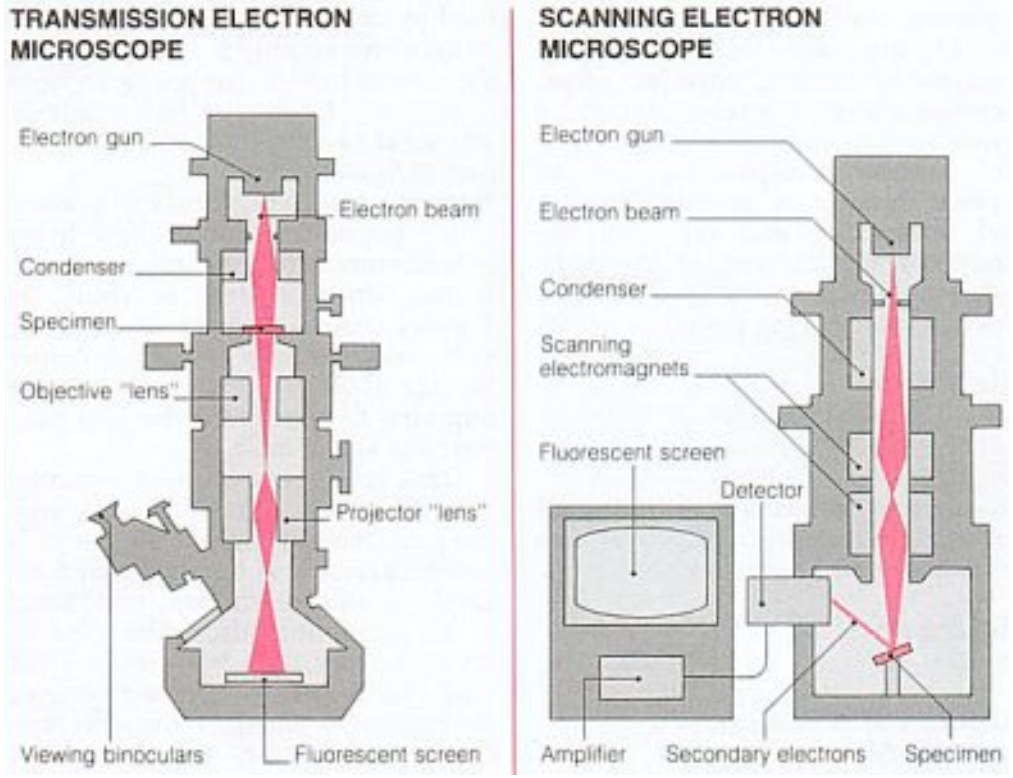
- Interaction of electrons with surface
- Source of electrons – cathode – thermoemission, field-emission
- Focusing lens for electron beam

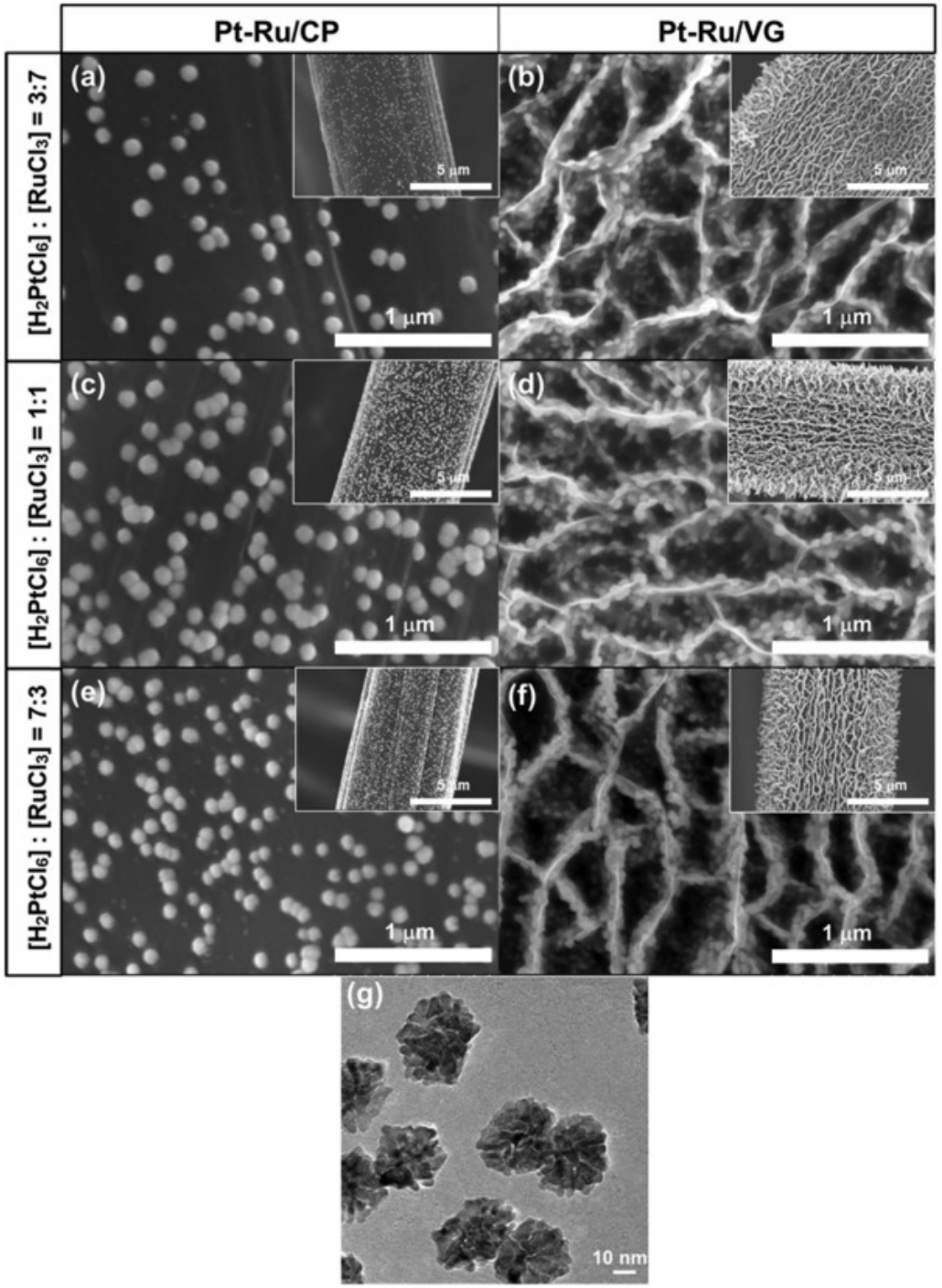
  1. SEM

- Electron beam energy: 0.2 – 40 keV; scanning the surface
- Detection of secondary electrons + backscattered electrons (topography); photons of characteristic x-ray (chemical composition); light (luminiscence – special phases)
- Penetration depth vs. substrate and layer thickness
- High vacuum vs. ESEM
- Resolution ≈ tens of nm

2. TEM

- Energy of electron beam
- Detection of transmitted electrons – CCD camera/fluorescence screen; bright field + dark field; diffraction; electron energy loss (chemical composition); 3D imaging
- Thin specimen; high vacuum
- Resolution ≈ Å
- HRTEM: higher energy of beam; thin specimen; UHV; resolution 0.05nm

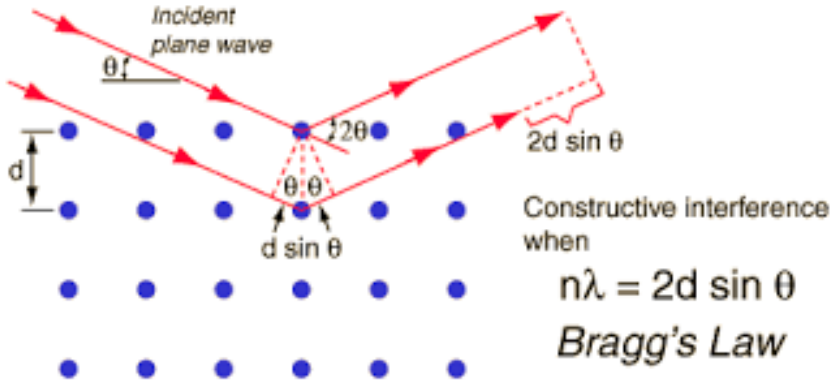


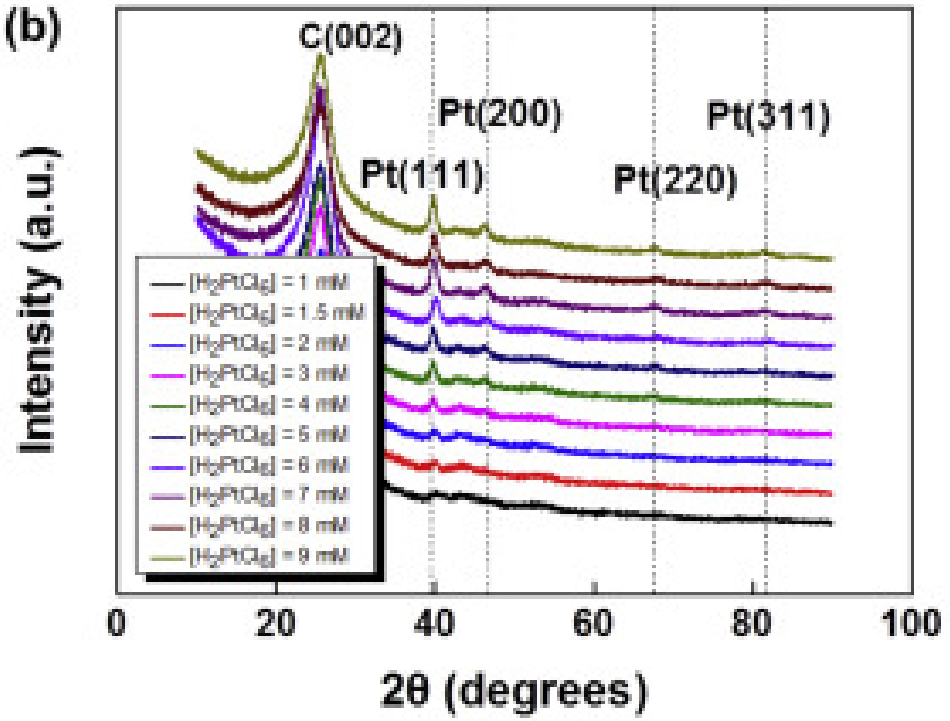


- SEM images of Pt–Ru/CP and Pt–Ru/VG obtained from three typical electrolyte compositions. (a) and (b) [H2PtCl6]:[RuCl3] = 3:7, average catalyst diameter: 103.5 ± 3.1 nm and 46.3 ± 1.5 nm; (c) and (d) [H2PtCl6]:[RuCl3] = 1:1, average catalyst diameter: 111.1 ± 2.8 nm and 51.2 ± 1.8 nm; (e) and (f) [H2PtCl6]:[RuCl3] = 7:3, average catalyst diameter: 98.3 ± 1.9 nm and 45.9 ± 1.1 nm. Insets: SEM images with a smaller magnification. (g) HRTEM image of Pt–Ru/VG obtained from the electrolyte composition of [H2PtCl6]:[RuCl3] = 1:1.

X-ray diffraction (XRD)

- Interaction of X-rays with the specimen
- Diffraction according to Bragg's law
- Source of X-rays – termoemission + single crystal diffraction on Cu (CuKα source with λ = 0.15425nm)
- Detection of diffracted X-rays
- Sample rotates in a path of collimated incident X-ray beam at angle θ + detector collects the X-rays at 2θ
- Observation of phases coexistence; crystallinity; lattice parameters

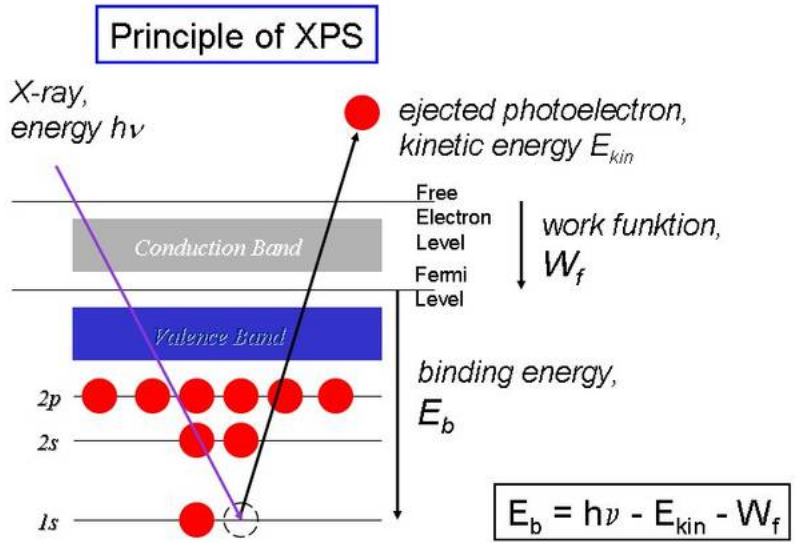


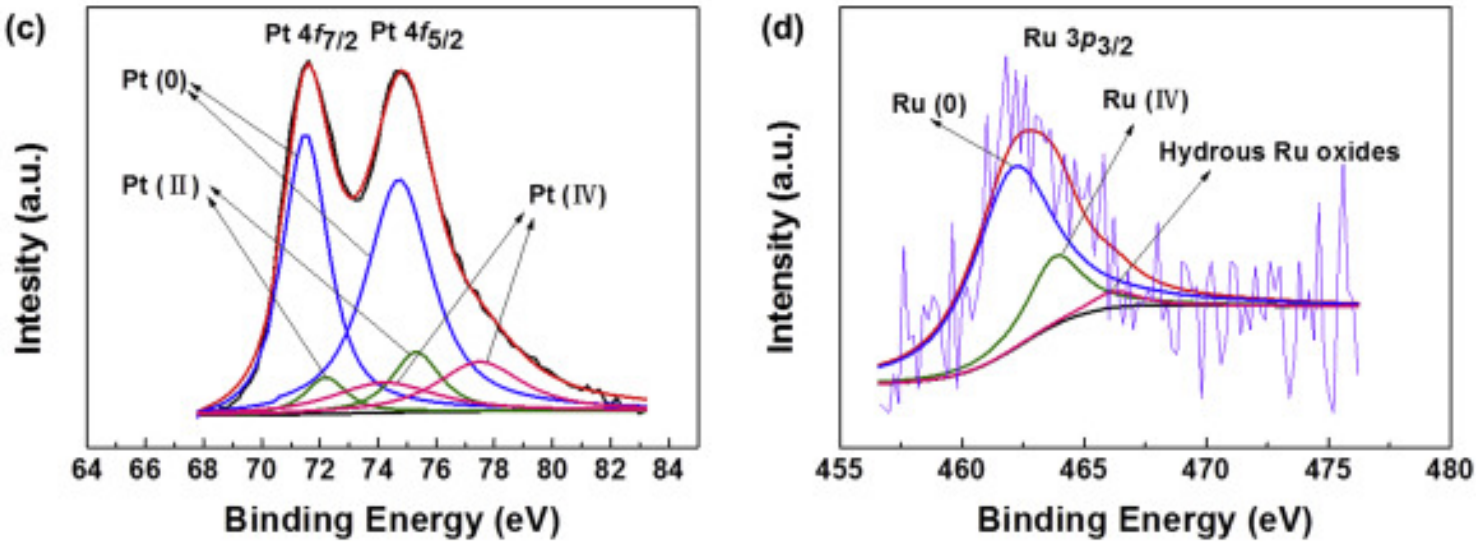


- XRD patterns of Pt–Ru/VG obtained from different electrolyte compositions

X-ray photoelectron spectroscopy (XPS)

- Interaction of X-rays with specimen
- X-ray sources: Kα Al (monochromatic); Kα Mg (non-monochromatic)
- Detecting the ecsaped photoelectrons (amount + carrying the information about binding energy)
- Observation of chemical composition; chemical state; surface contamination/ surface functionalization; empirical formula; depth analysis (if equipped with ion beam etching)
- HV/UHV required; starting at Li; surface sensitive (few nm); difficult fitting (overlapping peaks); limited size of samples

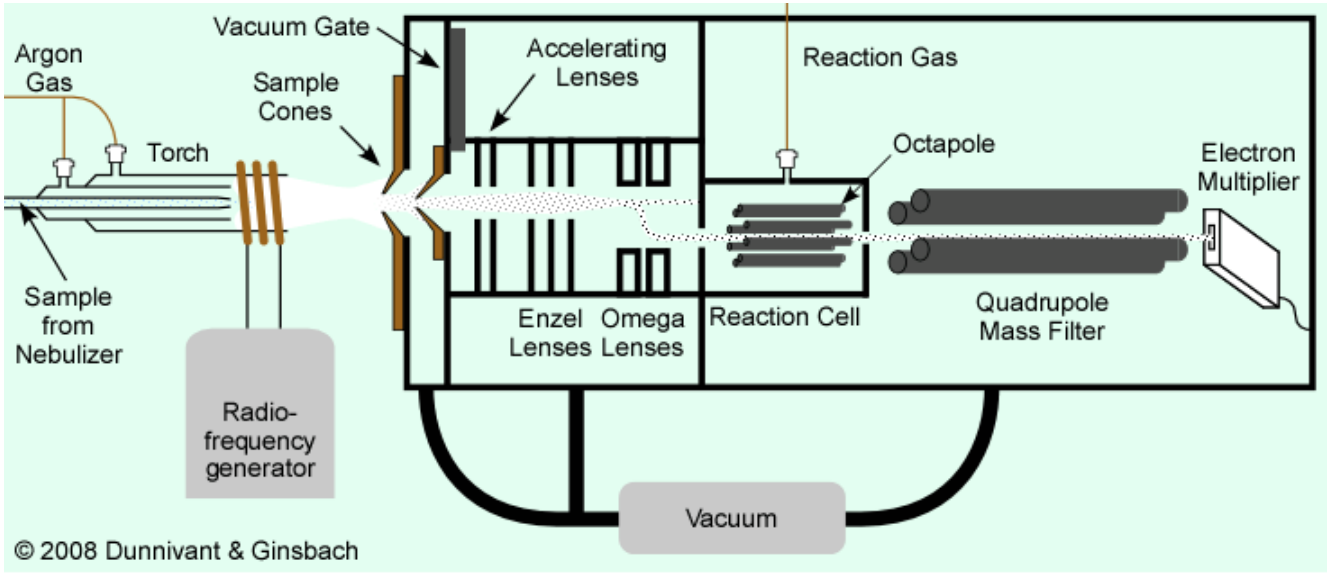


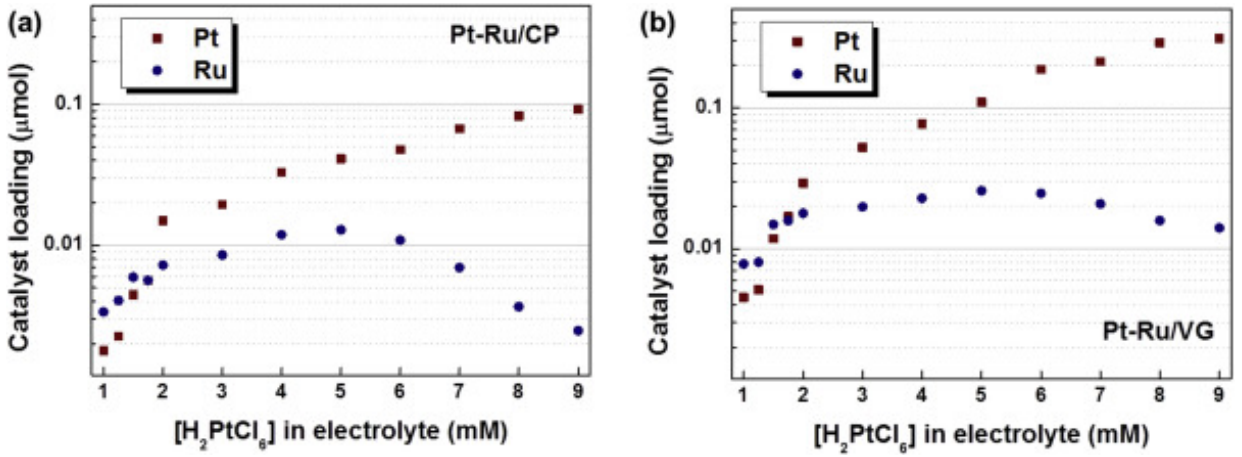


- (c) Pt 4f XPS spectra and (d) Ru 3p XPS spectra of the catalyst Pt–Ru/VG with a precursor of [H2PtCl6]:[RuCl3] = 1:1

Inductively coupled plasma mass spectrometry (ICP-MS)

- Introduction of analyte to plasma (solid - laser ablation; gas – direct; liquid – direct)
- Ionization of analyte in plasma (other methods: MALDI; electrospray; thermospray; chemical ionization; field desorption)
- Separation of ions based on m/z (quadrupole; octapole; sector separator; TOF; ion trap)
- Detection of ionized molecules/fragments/particles (induced charge; produced current)
- Qualitative and quantitative (if calibrated) technique





- Pt and Ru loadings on (a) pristine CP and (b) VG-coated CP with a varying electrolyte composition

Results

1. Introducing VG – increasing of

- Loading mass of Pt and Ru; catalytic stability; catalytic activity

2. introducing VG – decreasing of

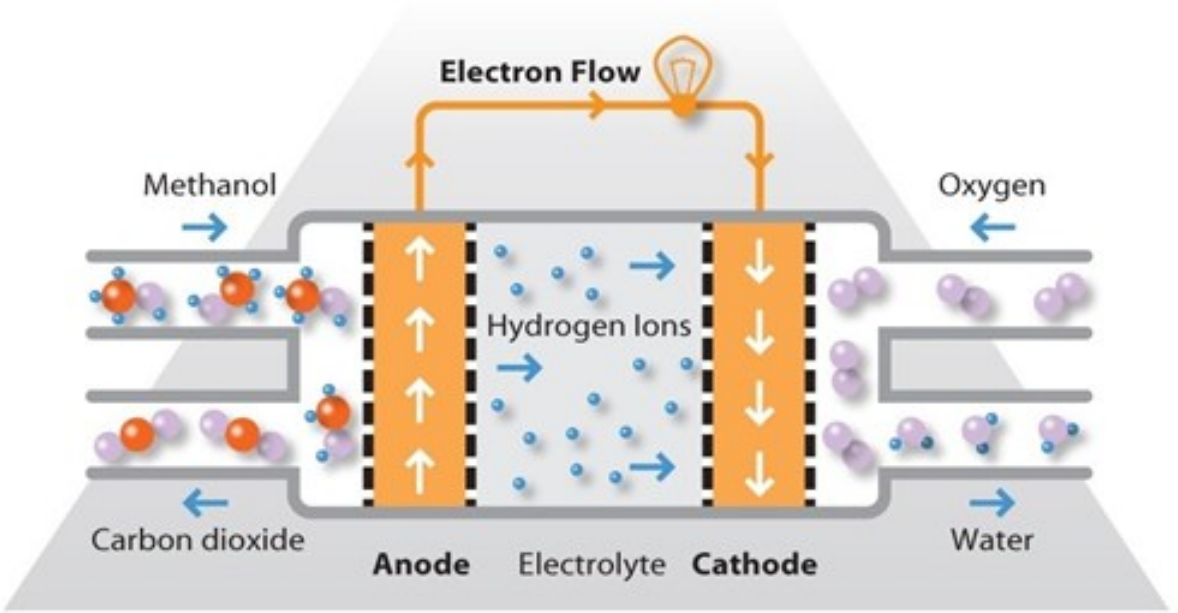
- Size of Pt, Ru nanoparticles

3. analysis

- SEM + HRTEM – size of graphene
- XRD – Pt in fcc, however Ru absent
- XPS – oxidation number for Pt, Ru unproven (non-monochromatic source – lower resolution)

4. what to improve

- Presentation of mass spectra
- Evidence of presence of Ru
- Hydrogen content/contamination of VG; Pt-Ru/VG



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