

# Hybrid catalytic systems for the electrooxidation of dimethyl ether in acid media.

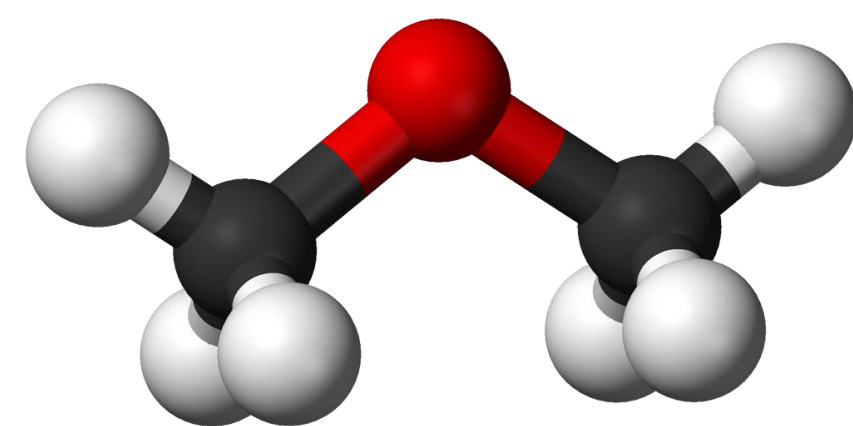


Beata Rytelawska, Iwona A. Rutkowska (supervisor), Paweł J. Kulesza (tutor)

Faculty of Chemistry, University of Warsaw, Poland

Electrocatalytic activity of Vulcan-supported PtSn (PtSn/V) nanostructured alloys toward electrooxidation of dimethyl ether (DME), a potential small-organic-molecule fuel, has been significantly enhanced in acid medium ( $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ) by decorating PtSn/V with ruthenium black or bimetallic PtRu nanoparticles. The enhancement effect concerns both shifting the onset potential for the DME-oxidation toward less positive values and increase of the DME electrocatalytic current densities recorded under both cyclic voltammetric and chronoamperometric conditions. The activating capabilities of ruthenium nanostructures seem to originate from the existence (even below  $0.45 \text{ V vs. RHE}$ ) of reactive ruthenium oxo/hydroxo groups on their surfaces capable of inducing the oxidative removal of poisoning (CO type) adsorbates from the neighboring platinum catalytic sites. In this respect, the Ru-oxo species seem to support activity of Sn forming with Pt the PtSn heterogeneous alloy. The Ru-decorated PtSn/V and, in particular, PtSn/V admixed with PtRu exhibit very high activity toward the oxidation of methanol which is also an important DME-oxidation intermediate. On the whole, the hybrid materials composed of Vulcan-supported PtSn decorated with Ru or PtRu nanoparticles seem to act as multifunctional nanoreactors inducing not only stripping of poisoning adsorbates but also catalyzing oxidation of the DME-reaction intermediates (methanol).

## Dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) as alternative fuel

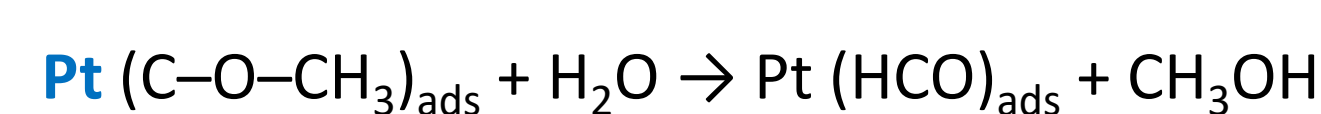
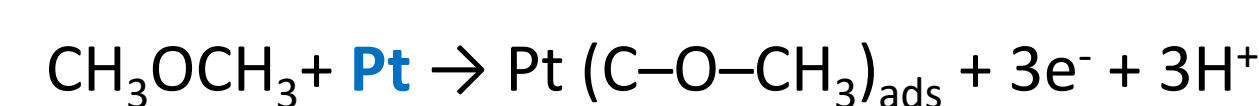


- lower emission of  $\text{NO}_x$  i  $\text{SO}_x$
- easy to obtain
- cheaper than MeOH
- non-toxic
- high specific energy:  $8.2 \text{ kWh/kg}$  ( $12\text{e}^-$ )
- non spreadable into groundwater
- decomposable in atmosphere within tens of hours

**Mechanistic aspects during electrooxidation: C-H bond breaking (dehydrogenation) and C-O-C bond breaking (but CO formation and poisoning of metal catalytic surfaces)**

## Mechanism of dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) electrooxidation

Activity of Pt and Ru components during  $\text{CH}_3\text{OCH}_3$  oxidation:

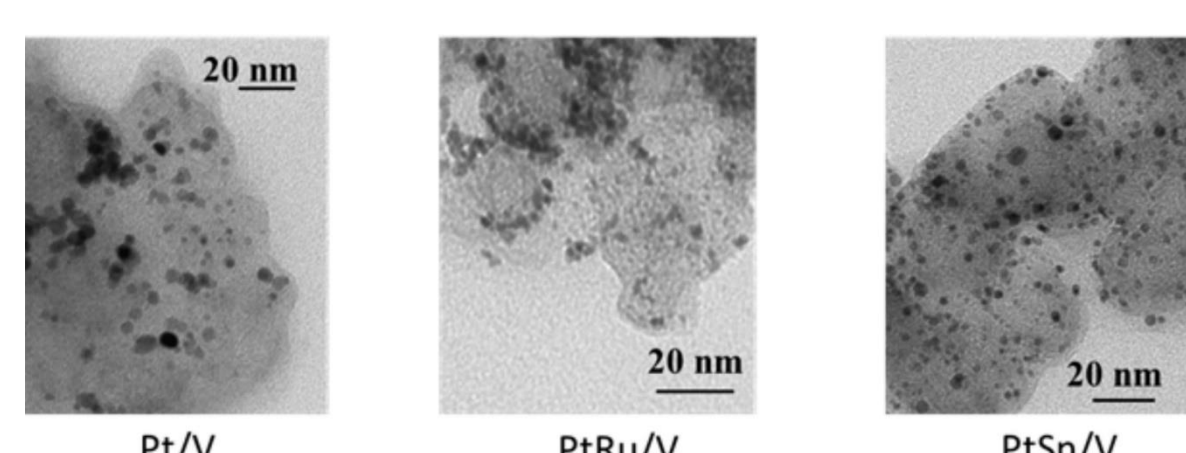


**PtRu - common electrocatalyst for methanol ( $\text{CH}_3\text{OH}$ ) oxidation.**

**Poisoning CO adsorbates appear as intermediates.**

Second metal component (Ru or Sn) tends to facilitate the oxidative removal of poisoning adsorbates.

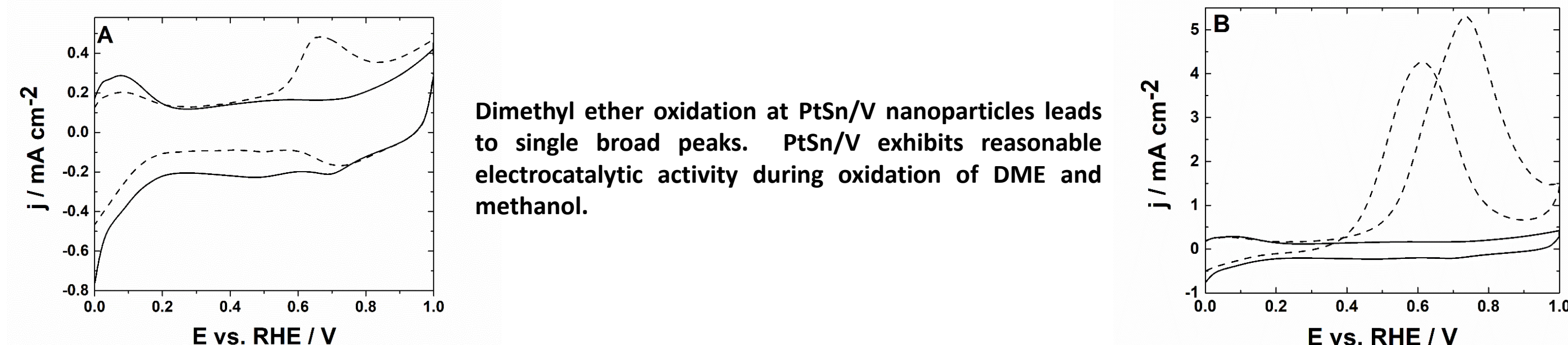
## Microscopic identity of noble-metal-based catalytic centers



TEM images of Vulcan-supported Pt (Pt/Vulcan), PtRu (PtRu/Vulcan) and PtSn (PtSn/Vulcan) catalytic nanoparticles.

The noble metal nanoparticles (Pt, PtRu, and PtSn), which are immobilized on Vulcan carriers, have sizes on the level of 2-3 nm. Metal nanoparticles tend to agglomerate to form centers ranging from ca. 7 to 15 nm.

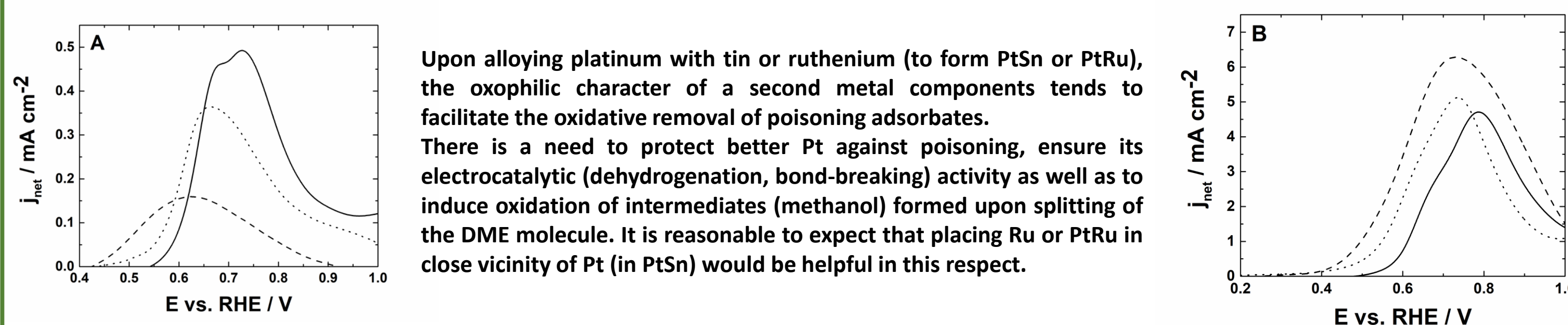
## Electrooxidation of dimethyl ether and methanol at PtSn/Vulcan



Dimethyl ether oxidation at PtSn/V nanoparticles leads to single broad peaks. PtSn/V exhibits reasonable electrocatalytic activity during oxidation of DME and methanol.

(A) Voltammetric responses recorded in absence (solid line), and in presence of DME at bare PtSn/V nanoparticles (dotted line). (B) Cyclic voltammetric responses recorded in absence (solid line) and presence (dashed line) of methanol at PtSn/V. Electrolyte, deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . Electrode substrate, glassy carbon. PtSn loading,  $75 \mu\text{g cm}^{-2}$  (Pt-metal loading,  $15 \mu\text{g cm}^{-2}$ ).

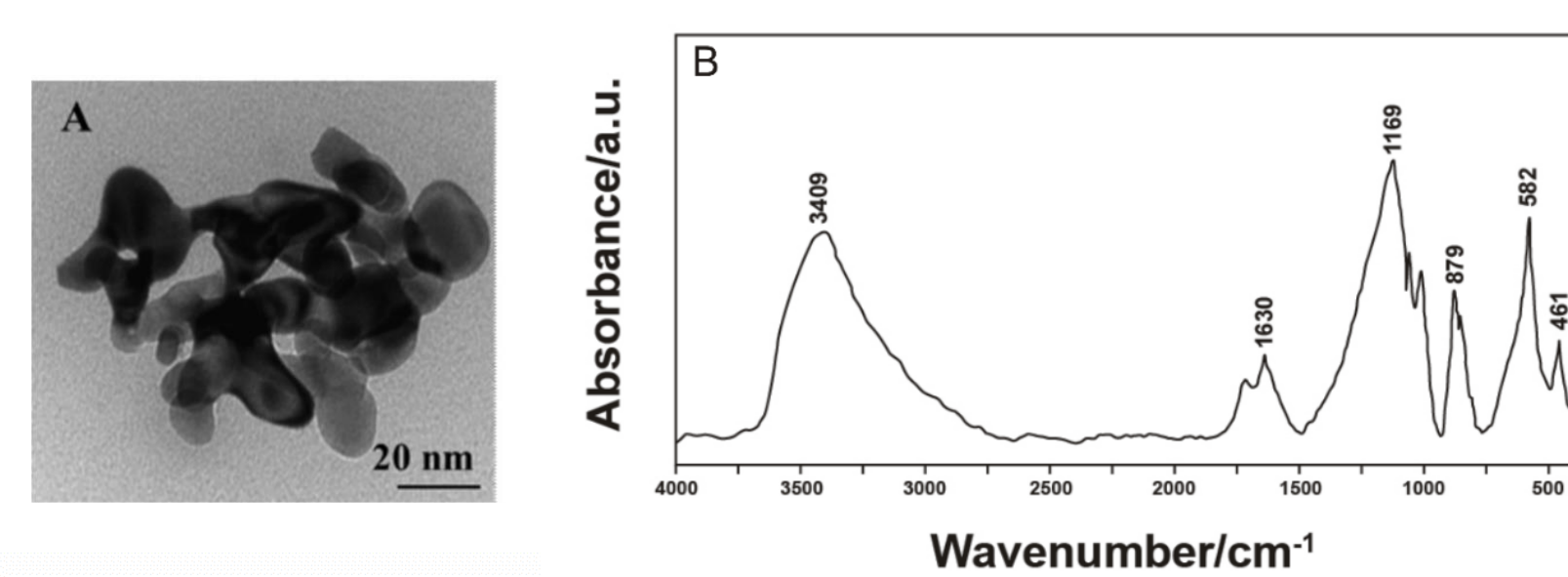
## Background-subtracted electrooxidation of dimethyl ether and methanol at Pt/Vulcan, PtRu/Vulcan and PtSn/Vulcan



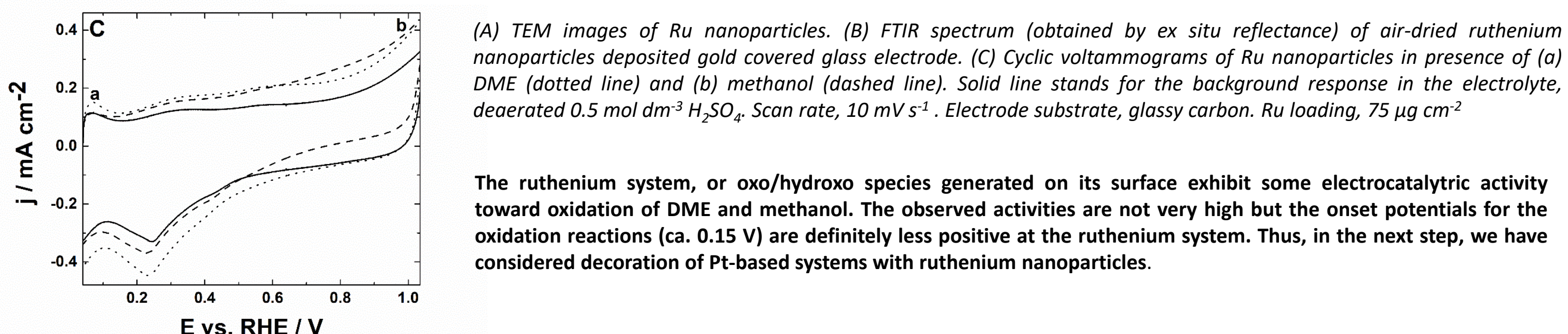
Upon alloying platinum with tin or ruthenium (to form PtSn or PtRu), the oxophilic character of a second metal component tends to facilitate the oxidative removal of poisoning adsorbates. There is a need to protect better Pt against poisoning, ensure its electrocatalytic (dehydrogenation, bond-breaking) activity as well as to induce oxidation of intermediates (methanol) formed upon splitting of the DME molecule. It is reasonable to expect that placing Ru or PtRu in close vicinity of Pt (in PtSn) would be helpful in this respect.

Background-subtracted (net) (A) DME-oxidation currents recorded at Pt/V (solid line), PtRu/V (dashed line) and PtSn/V (dotted line); and (B) methanol oxidation currents recorded at Pt/V (solid line), PtRu/V (dashed line) and PtSn/V (dotted line). Electrolyte, deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . Electrode substrate, glassy carbon. Pt-metal loading,  $15 \mu\text{g cm}^{-2}$ .

## Performance of ruthenium-black nanoparticles

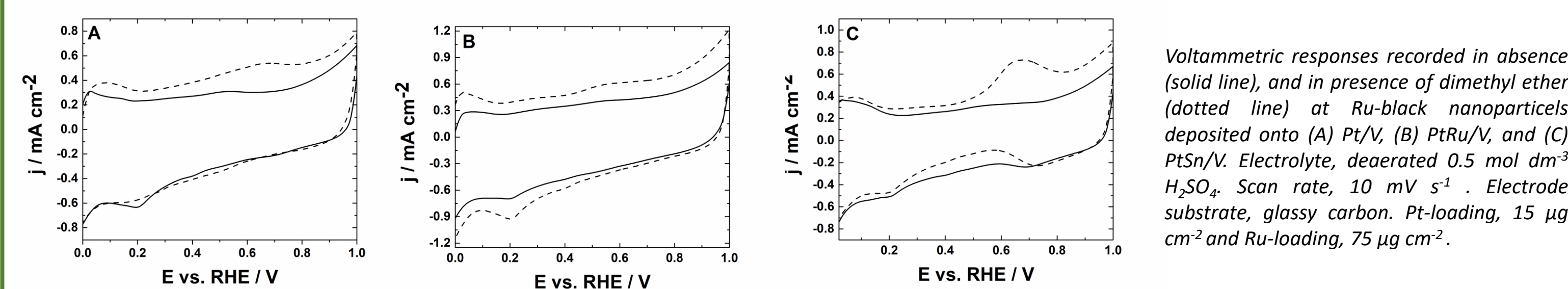


The bands at  $461 \text{ cm}^{-1}$  and  $582 \text{ cm}^{-1}$  shall be attributed to asymmetric stretching modes of ruthenium-oxide-type species. The peak at  $879 \text{ cm}^{-1}$  reflects the presence of Ru-OH groups. The band appearing around at  $1169 \text{ cm}^{-1}$  can be correlated with the stretching vibration of peroxo groups and band at around  $1630 \text{ cm}^{-1}$  to the vibration of hydroxyl groups of molecular. The broad band at  $3409 \text{ cm}^{-1}$  stands most likely for the stretching vibrations of OH groups.



The ruthenium system, or oxo/hydroxo species generated on its surface exhibit some electrocatalytic activity toward oxidation of DME and methanol. The observed activities are not very high but the onset potentials for the oxidation reactions (ca.  $0.15 \text{ V}$ ) are definitely less positive at the ruthenium system. Thus, in the next step, we have considered decoration of Pt-based systems with ruthenium nanoparticles.

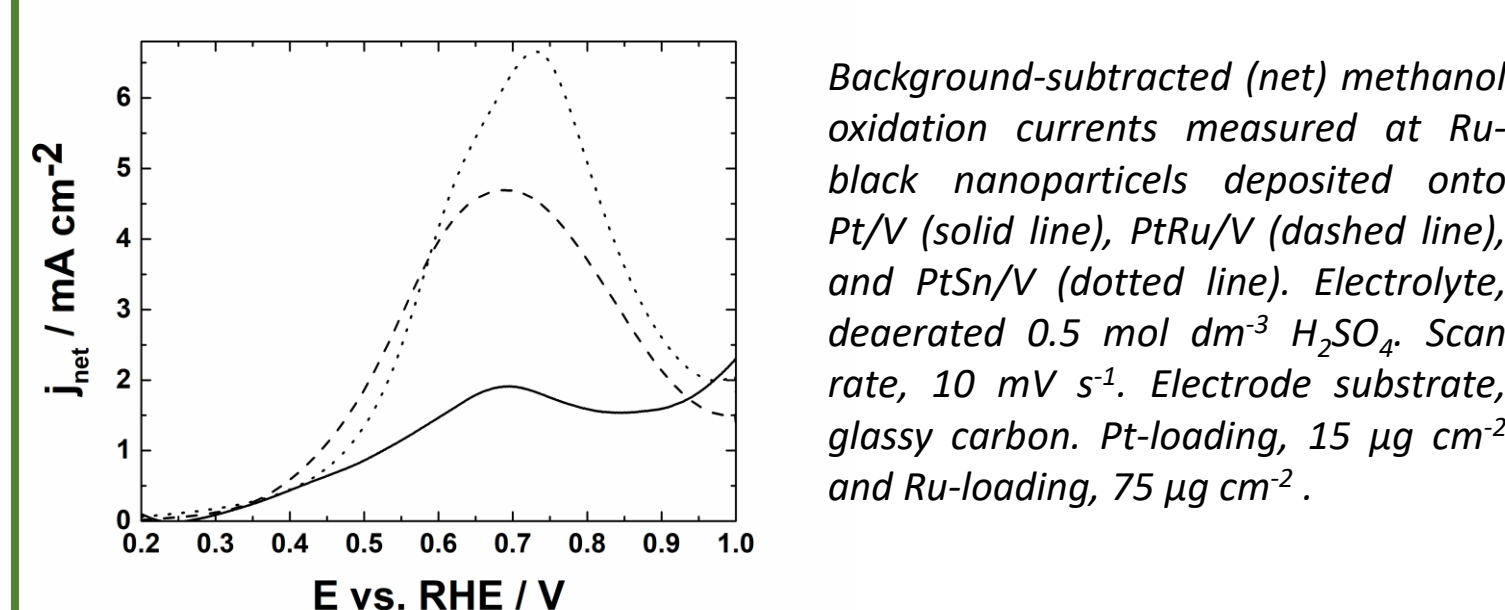
## Electrooxidation of dimethyl ether at Pt/Vulcan, PtRu/Vulcan and PtSn/Vulcan decorated with ruthenium black



Voltammetric responses recorded in absence (solid line), and in presence of dimethyl ether (dotted line) at Ru-black nanoparticles deposited onto (A) Pt/V, (B) PtRu/V, and (C) PtSn/V. Electrolyte, deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . Electrode substrate, glassy carbon. Pt-loading,  $15 \mu\text{g cm}^{-2}$  and Ru-loading,  $75 \mu\text{g cm}^{-2}$ .

Addition of Ru to the electrocatalytic interface can enhance the activity of Pt sites during oxidation of DME due to the ability of ruthenium to form chemisorbed oxide or OH species at significantly lower potentials than platinum

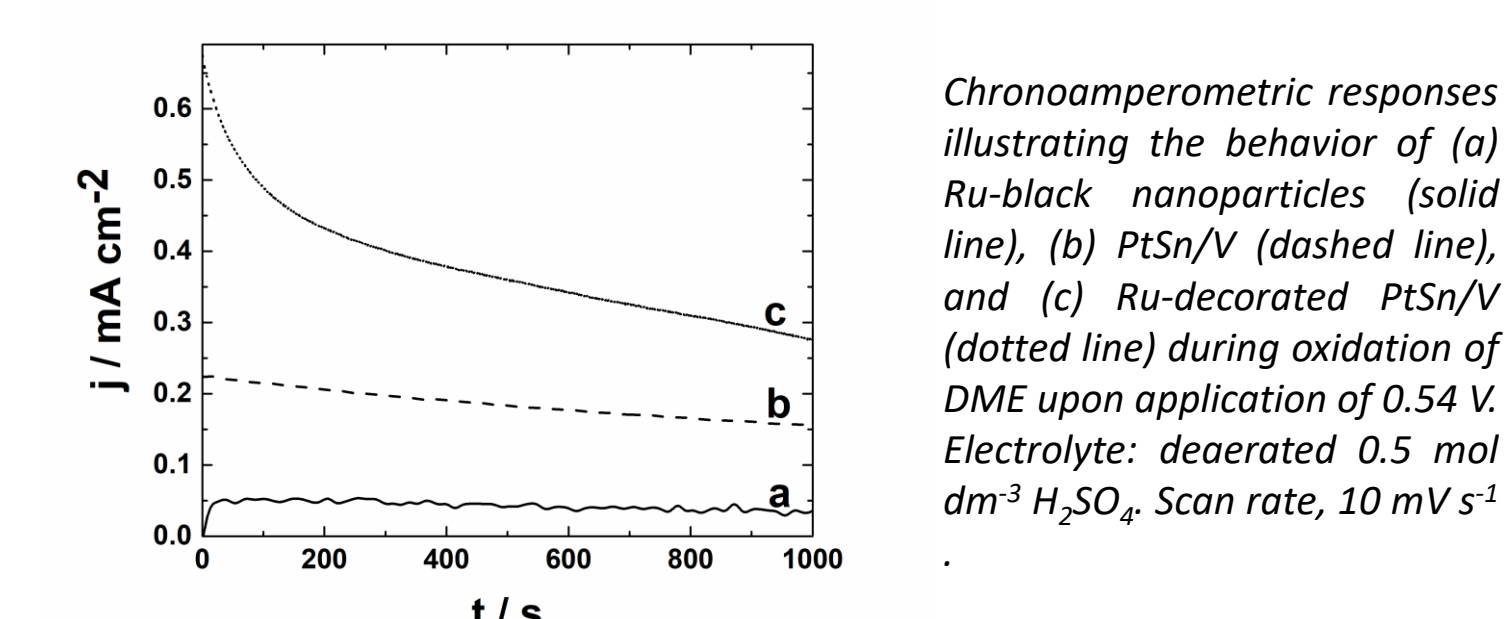
## Electrooxidation of methanol at Ru-black nanoparticles deposited onto Pt/Vulcan, PtRu/Vulcan and PtSn/Vulcan



Background-subtracted (net) methanol oxidation currents measured at Ru-black nanoparticles deposited onto Pt/V (solid line), PtRu/V (dashed line), and PtSn/V (dotted line). Electrolyte, deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . Electrode substrate, glassy carbon. Pt-loading,  $15 \mu\text{g cm}^{-2}$  and Ru-loading,  $75 \mu\text{g cm}^{-2}$ .

Decoration with Ru nanoparticles shifts the onset potential for the oxidation of methanol toward less positive values. The methanol-oxidation enhancement effect seems to be the most pronounced in the case of Ru-decorated PtSn/V. Decoration with Ru, or more precisely the exposure of Pt-based catalysts to Ru-oxo species existing on Ru surfaces, leads to the activation of Pt thorough chemical interactions with RuOH or RuOx inducing removal of poisoning adsorbates.

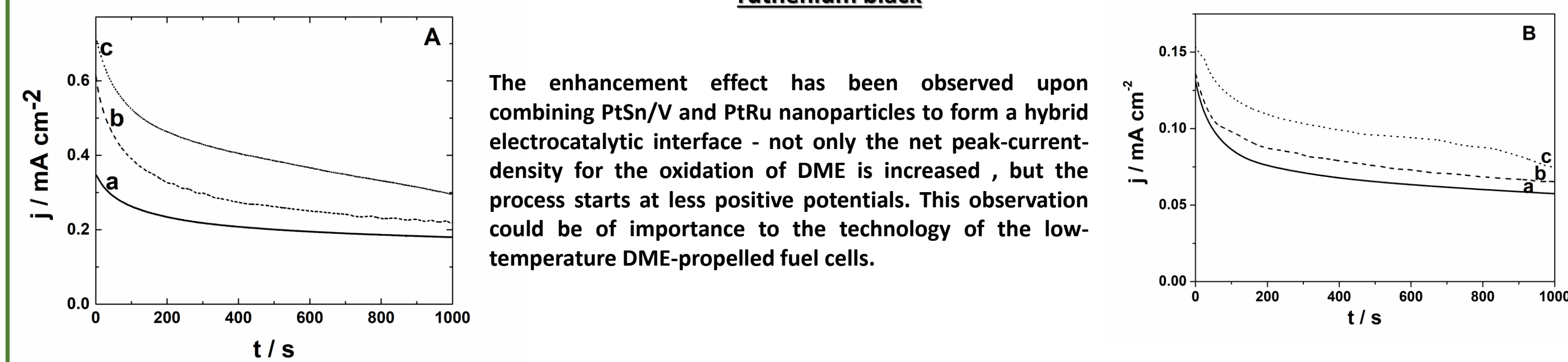
## Chronoamperometric diagnostic experiments dimethyl ether oxidation at Ru-black, PtSn/Vulcan and PtSn/Vulcan decorated with ruthenium black



Chronoamperometric responses illustrating the behavior of (a) Ru-black nanoparticles (solid line), (b) PtSn/V (dashed line), and (c) Ru-decorated PtSn/V (dotted line) during oxidation of DME upon application of  $0.54 \text{ V}$ . Electrolyte: deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$

The hybrid Ru-containing system exhibits the current density ( $0.28 \text{ mA cm}^{-2}$ ) larger than the sum of the analogous currents yielded by single components, Ru ( $0.035 \text{ mA cm}^{-2}$ ) and PtSn/V ( $0.155 \text{ mA cm}^{-2}$ ) It is reasonable to postulate a synergistic enhancement effect in the case of the decoration of PtSn/V with Ru during oxidation of DME

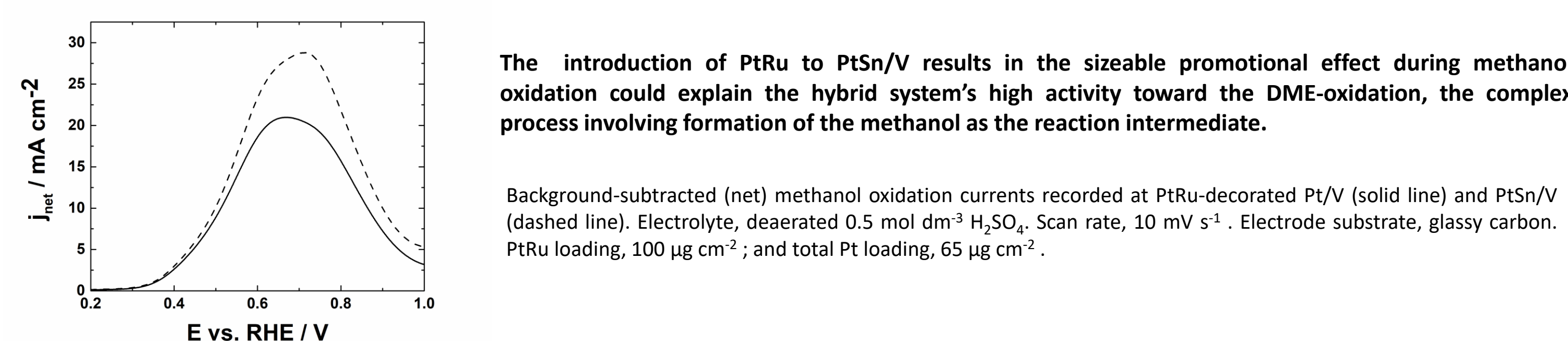
## Chronoamperometric diagnostic experiments: dimethyl ether oxidation at Pt/Vulcan, PtRu/Vulcan and PtSn/Vulcan decorated with ruthenium black



The enhancement effect has been observed upon combining PtSn/V and PtRu nanoparticles to form a hybrid electrocatalytic interface - not only the net peak-current-density for the oxidation of DME is increased, but the process starts at less positive potentials. This observation could be of importance to the technology of the low-temperature DME-propelled fuel cells.

Chronoamperometric responses illustrate the performance of Ru-black nanoparticles deposited onto (a) Pt/V (solid line), (b) PtRu/V (dashed line), and (c) PtSn/V (dotted line) during oxidation of DME upon application of (A)  $0.54 \text{ V}$  and (B)  $0.44 \text{ V}$ . Electrolyte: deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ .

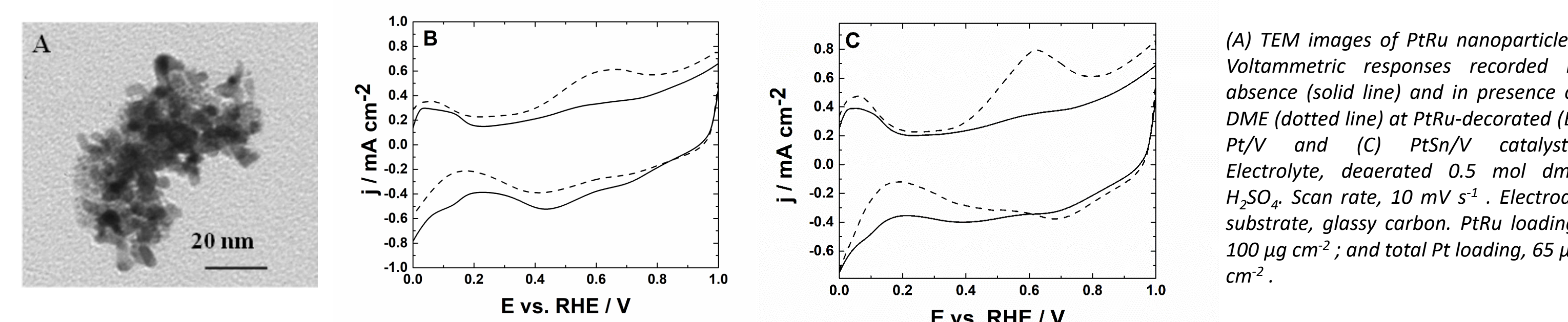
## Electrooxidation of methanol at Pt/Vulcan and PtRu/Vulcan decorated with PtRu-black nanoparticles



The introduction of PtRu to PtSn/V results in the sizeable promotional effect during methanol oxidation could explain the hybrid system's high activity toward the DME-oxidation, the complex process involving formation of the methanol as the reaction intermediate.

Background-subtracted (net) methanol oxidation currents recorded at PtRu-decorated Pt/V (solid line) and PtSn/V (dashed line). Electrolyte, deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . Electrode substrate, glassy carbon. PtRu loading,  $100 \mu\text{g cm}^{-2}$ ; and total Pt loading,  $65 \mu\text{g cm}^{-2}$ .

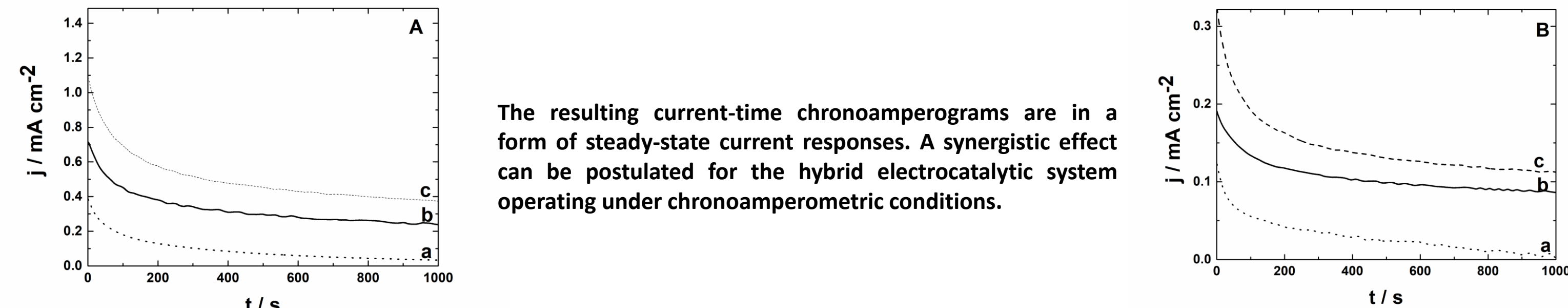
## Oxidation of dimethyl ether at Pt/Vulcan and PtSn/Vulcan decorated with PtRu nanoparticles



(A) TEM images of PtRu nanoparticles. Voltammetric responses recorded in absence (solid line) and in presence of DME (dotted line) at PtRu-decorated (B) Pt/V and (C) PtSn/V catalysts. Electrolyte, deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . Electrode substrate, glassy carbon. PtRu loading,  $100 \mu\text{g cm}^{-2}$ ; and total Pt loading,  $65 \mu\text{g cm}^{-2}$ .

The enhancement effect has been observed upon combining PtSn/V and PtRu nanoparticles to form a hybrid electrocatalytic interface - not only the net peak-current-density for the oxidation of DME is increased, but the process starts at less positive potentials. This observation could be of importance to the technology of the low-temperature DME-propelled fuel cells.

## Chronoamperometric diagnostic experiments: DME oxidation at Pt/Vulcan and PtSn/Vulcan decorated with PtRu nanoparticles



The resulting current-time chronoamperograms are in a form of steady-state current responses. A synergistic effect can be postulated for the hybrid electrocatalytic system operating under chronoamperometric conditions.

Chronoamperometric responses illustrating the performance of (a) PtRu nanoparticles (dotted line) and PtRu-decorated (b) Pt/V (solid line) and (c) PtSn/V (dashed line) during oxidation of DME upon application of (A)  $0.54 \text{ V}$  and (B)  $0.44 \text{ V}$ . Electrolyte: deaerated  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Scan rate,  $10 \text{ mV s}^{-1}$ . PtRu loading,  $100 \mu\text{g cm}^{-2}$ ; and total Pt loading,  $65 \mu\text{g cm}^{-2}$

## Conclusions:

- Decoration of Vulcan-supported PtSn, PtSn/Vulcan, with unsupported ruthenium or PtRu nanoparticles leads to the enhancement of the PtSn/Vulcan system's catalytic activity toward electrooxidation of dimethyl ether (DME).
- The ruthenium additive to PtSn supports activity of the tin component within the alloy toward the oxidative removal of the inhibiting adsorbates (reaction intermediates) from the catalytic Pt sites, which are largely metallic as PtSn is heterogeneous alloy rather than intermetallic system.
- The multicomponent systems composed of PtSn/Vulcan and Ru or PtRu nanoparticles form multifunctional electrocatalytic nanoreactors.
- The onset potential for the oxidation of dimethyl ether (DME) is somewhat shifted toward less positive potentials, both in the presence of Ru and PtRu, seems to be of potential importance to the low-temperature fuel cell technology.