Preparation and characterisation of Pt based electrocatalysts for PEM fuel cells

by

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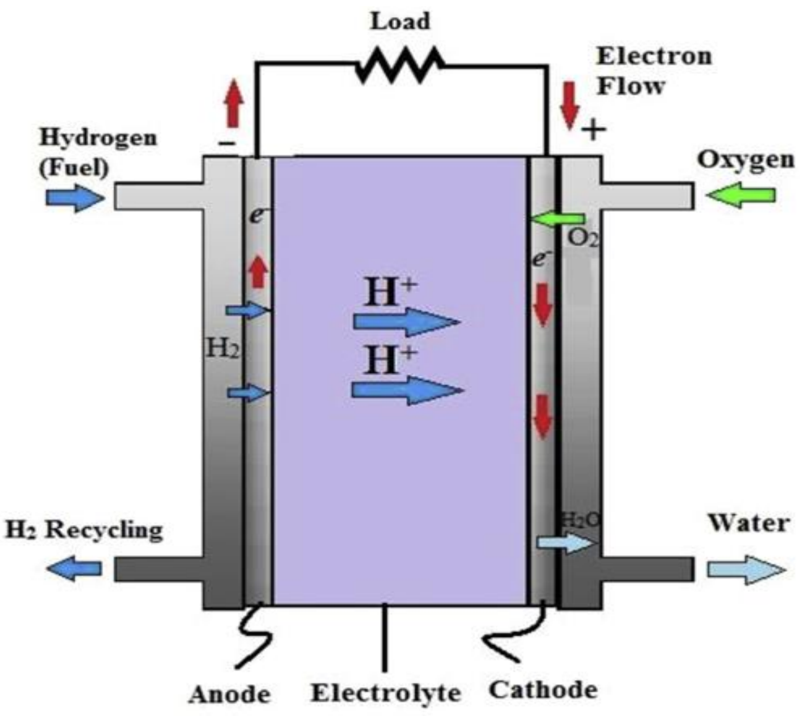
INSTITUTE OF MATERIALS AND ENVIRONMENTAL CHEMISTRY

2022

Polymer Electrolyte Membrane (PEM) Fuel Cells



Fuel cell half reactions:

Cathode: $\mathbf{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$

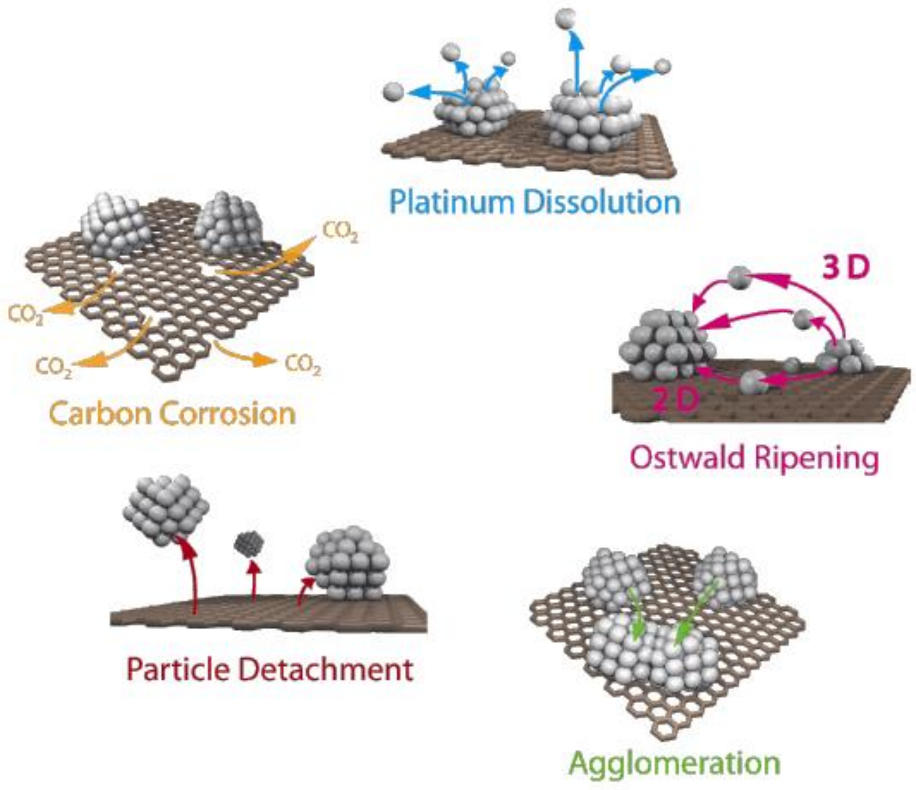
Anode: $\mathbf{H_2 \rightarrow 2H^+ + 2e^-}$

Commercially available catalyst:
Pt/carbon

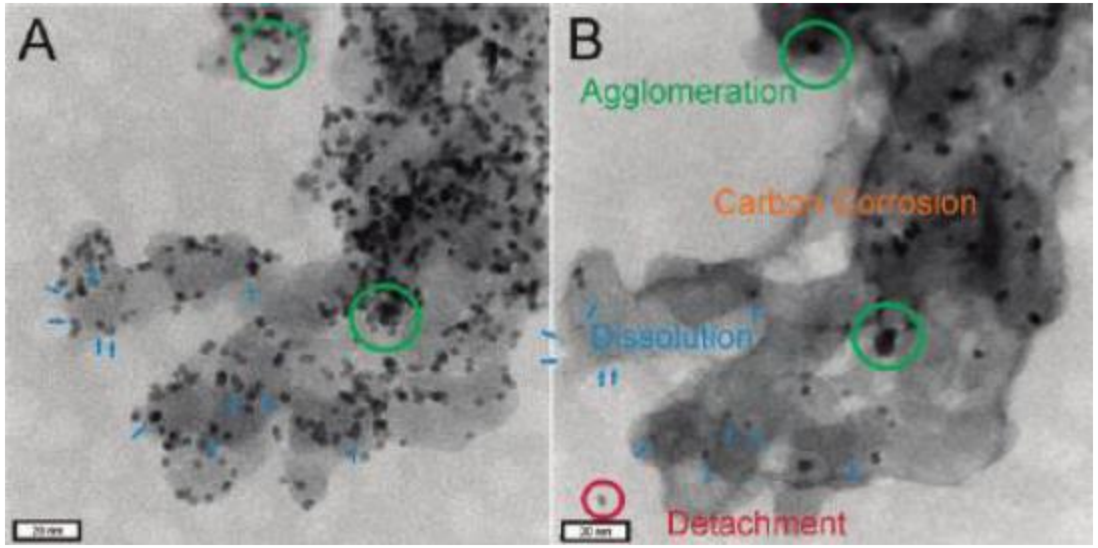
Drawbacks:
Pt is expensive,
Low CO-tolerance (H_2 from reformates → traces of CO),
Low resistance to corrosion of carbon support.

Benefits of PEMFCs:
Environmentally friendly,
Fast start-up,
Compact design,
Solidity of electrolyte.

Degradation of carbon supported platinum (Pt/C) catalyst



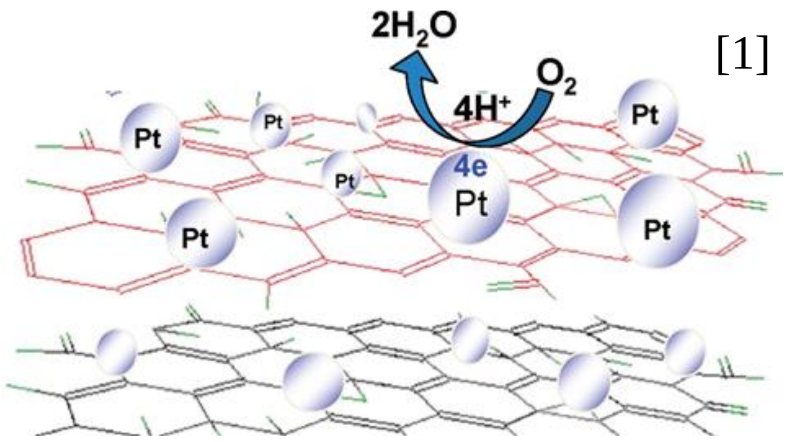
Possibilities of degradation of carbon-supported platinum particles [1]



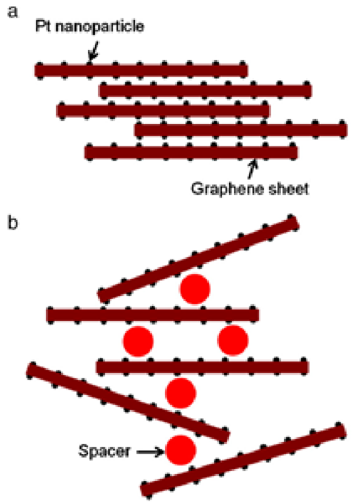
Degradation of Pt/C (Vulcan) fuel cell catalyst under simulated start-stop conditions. IL-TEM (Identical location transmission electron microscopy) images [2]

[1] J.C. Meier, C. Galeano, I. Katsounaros, et al, Beilstein J. Nanotechnol. 2014, 5, 44–67. doi:10.3762/bjnano.5.5
[2] J.C. Meier, C. Galeano, I. Katsounaros, et al., ACS Catal. 2012, 2, 832−843, dx.doi.org/10.1021/cs300024h

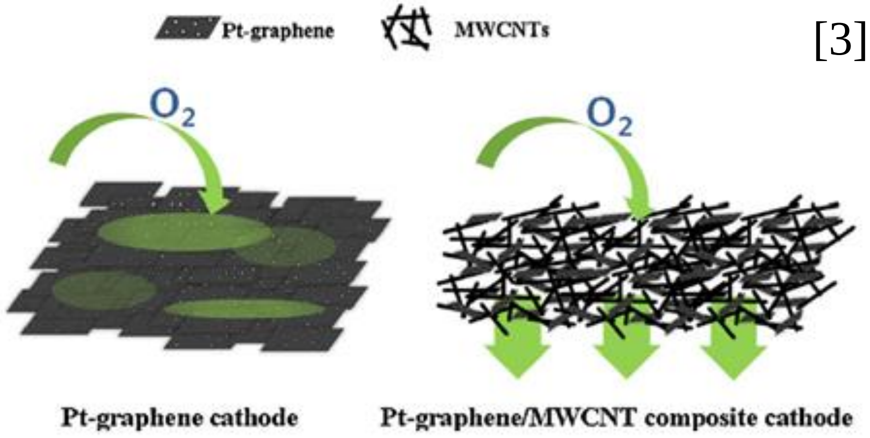
Use of novel carbonaceous materials (graphene derivatives, carbon nanotubes) as supports for fuel cells electrocatalyst



[1]



[2]



[3]

Advantages of graphene materials:

- Good stability
- Good conductivity

Disadvantage of graphene materials: 2D layers "stick together" → availability of Pt decreases → Pt utilization is low

Solution of the problem:

- Creating a 3D structure by inserting “spacers” [2];
- Mixing of 2D (graphene) and 1D (carbon nanotube) structures [3]

[1] B. Seger, P. V. Kamat, J. Phys. Chem. C 2009, 113, 7990–7995. https://doi.org/0.1021/jp900360
[2] S. Park, Y. Shao, H. Wan, et al. Electrochem. Commun., 2011, 13, 258–261. doi:10.1016/j.elecom.2010.12.028
[3] Y. S. Yun, D. Kim, Y. Tak and H. J. Jin, Synth. Met., 2011, 161, 2460–2465. doi:10.1016/j.synthmet.2011.09.030

Approach of the Renewable Energy Research Group

Key requirements for the design of PEMFC catalysts:

- Low Pt content and high metal dispersion;
- Highly CO tolerant anode electrocatalyst;
- High activity and selectivity in ORR for the cathode side catalyst;
- Increase of the conductivity and corrosion resistance of electrocatalysts by designing

Answers to challenges:

Novel composite structures for support [1] → increase of the stability → composite support from new type of carbonaceous materials

Mixed oxide - carbonaceous material composite supported Pt catalyst [1]

Incorporated Mo can not dissolve easily in the acidic media of PEMFC

Active metal

Conductivity; template for appropriate SSA

$$\mathbf{Pt/Ti_{0.8}Mo_{0.2}O_2\text{-}C}$$

Stability

CO tolerance for the supported Pt catalyst

C:

- Traditional carbonaceous materials (Black Pearls 2000, Vulcan XC-72R)
- New types of carbonaceous materials

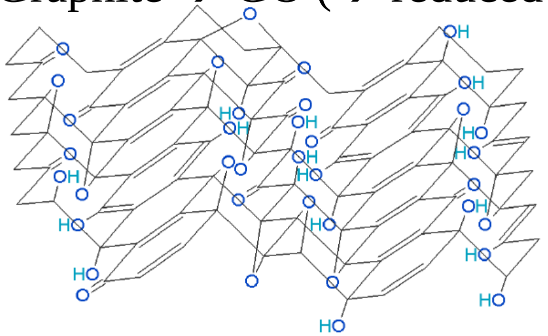
High temperature treatment: necessary for the Mo incorporation into rutile TiO_2

[1] I. Borbáth, E. Tálas, et al, Appl. Catal. A Gen. 2021, 620, 118155. https://doi.org/10.1016/j.apcata.2021.118155

New types of carbonaceous materials

Graphite oxide (GO)

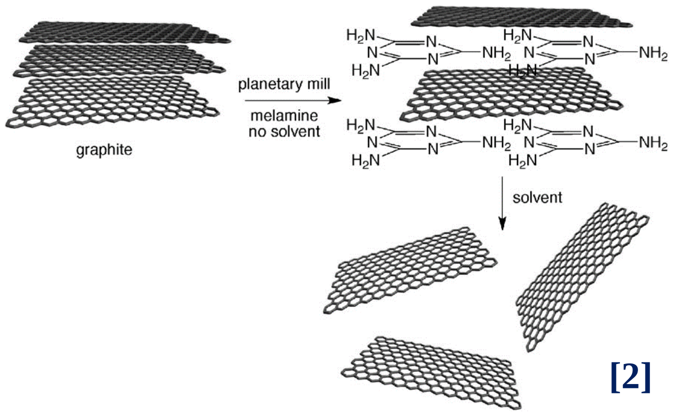
Graphite → GO (→ reduced graphene oxide (rGO))



[1]

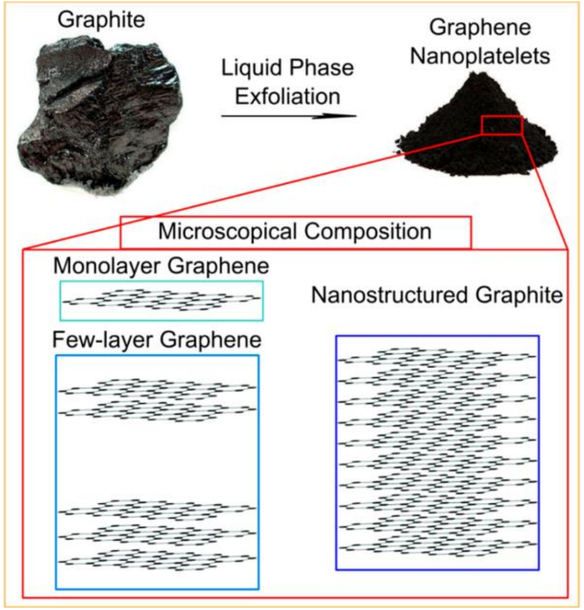
- Hydrophilic character relative to the parent graphite,
- Available in large amount

Multilayer graphene (MLG)



[2]

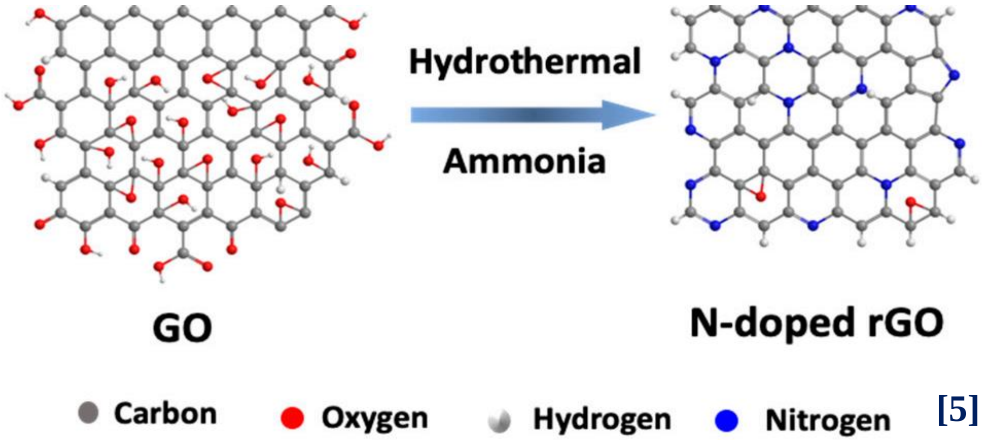
Graphene nanoplatelets (GNP)



[3]

- A mixture of single and few layer graphene and nanostructured graphite,
- Functional groups on the edges,
- Less hydrophilic,
- Inexpensive,
- Commercially available.

N-doped MLG [4], N-doped GO (NGr) [5]:



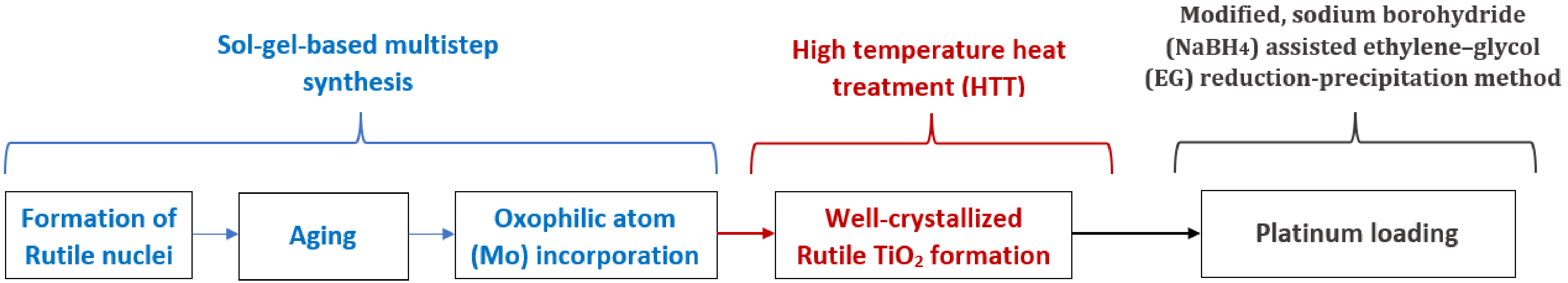
[5]

[1] T. Szabó, O. Berkesi, P. Forgó, et al, Chem. Mater. 2006, 18, 2740–2749.
[2] P. Cataldi, A. Athanassiou, I.S. Bayer, Appl. Sci. 2018, 8, 1438.
[3] V. Leon, M. Quintan, M.A. Herrero, J.L.G. Fierro, et al, Chem. Commun., 2011, 47, 10936–10938.
[4] M. Dan, A. Vulcu, S.A. Porav, et al, Molecules, 2021, 26, 3858. https://doi.org/10.3390/molecules26133858
[5] A. D. Smith, Q. Li, A. Vyas, et al, Sensors, 2019, 19, 4231; doi:10.3390/s19194231

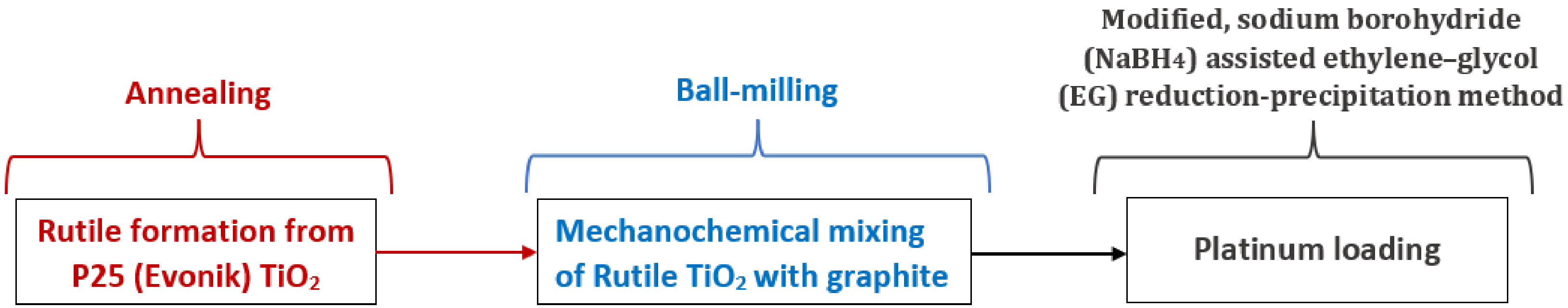
Experimental

Synthesis:

Sol-gel method:



Ball-milling method:



Physicochemical characterization

- **XRD** – crystalline structure of the oxide parts, Pt
- **XPS** – characterization of surface
- **Nitrogen physisorption** – specific surface area (SSA)
- **TEM** – platinum nanoparticles distribution on the surface

Electrochemical characterization

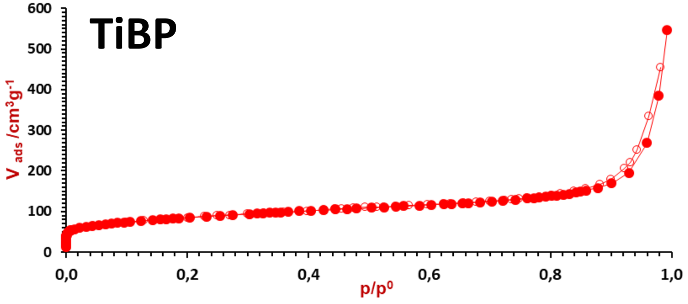
- **Cyclic voltammetry** – Electrochemical active surface area (ECSA), stability
- **CO_{ads}-stripping voltammetry** – CO tolerance

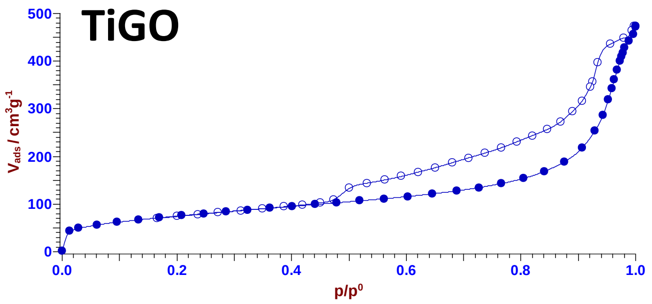
TiO_2-C composites
GO derived carbonaceous material

Preparation: sol-gel method

Support

Nitrogen physisorption



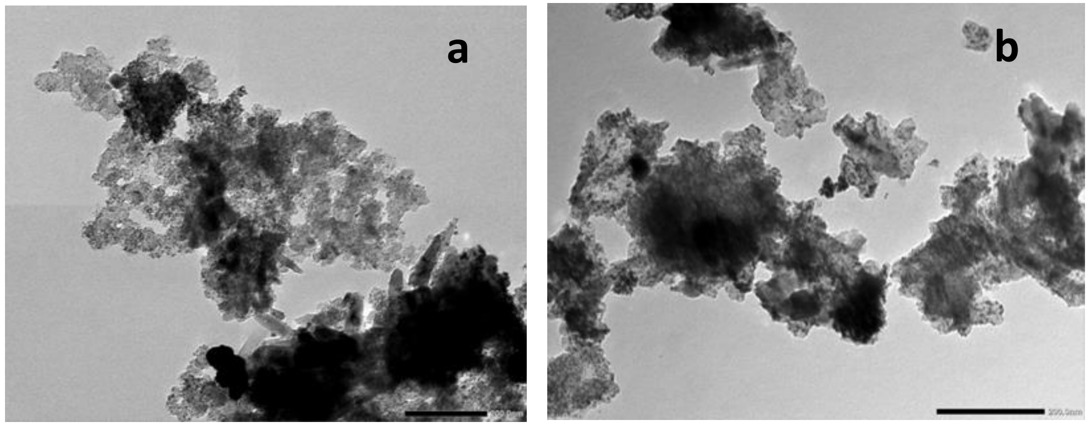


Sample ID	Support		Catalyst
	Pore volume, cm^3g^{-1}	BET surface area, m^2g^{-1}	Pt based on ICP, wt.%
TiBP (Pt/TiBP)	0.60	300	18.3
TiGO (Pt/TiGO)	0.69	264	18.2

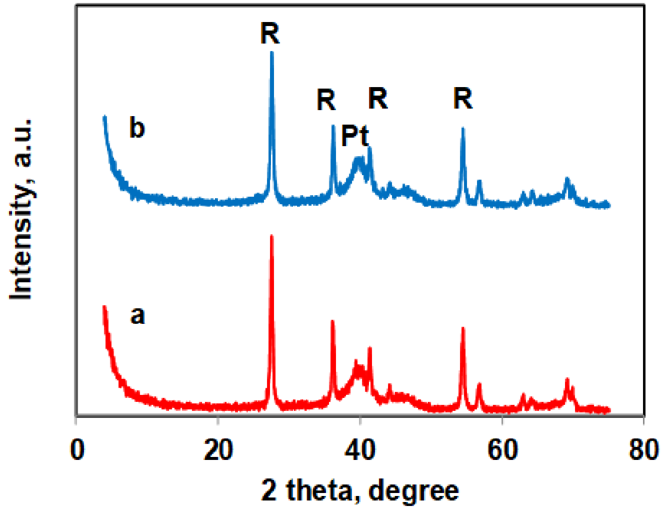
BP: Black Pearls 2000 (Cabot)

Electrocatalyst

TEM



XRD

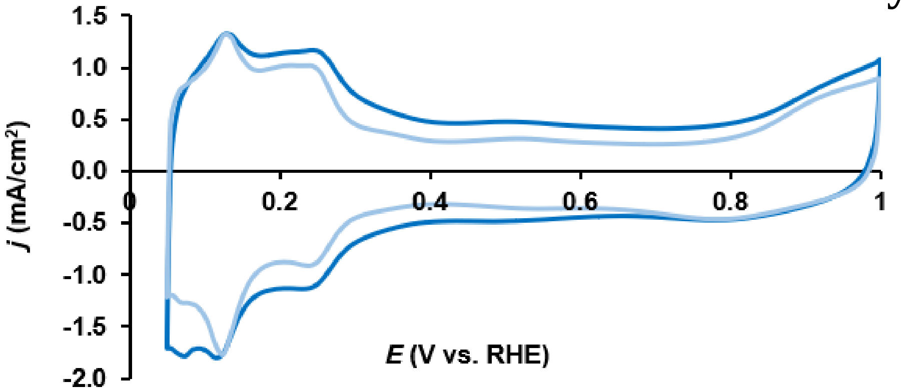


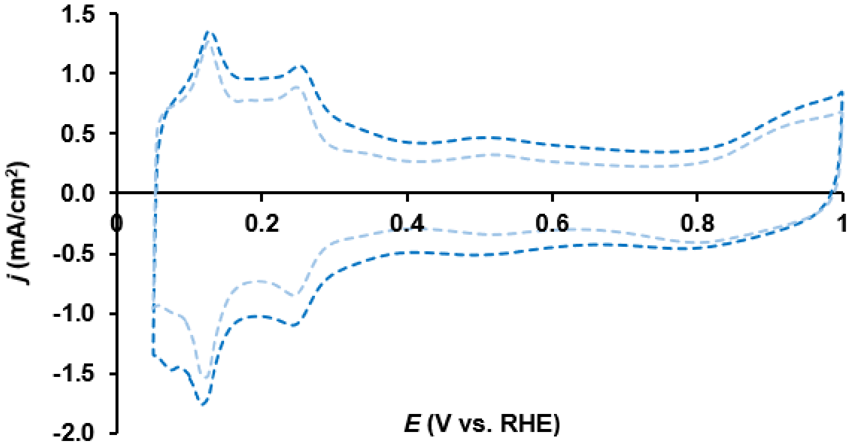
a: Pt/TiBP, b: Pt/TiGO, R: rutile.

Ref. I. Ayyubov, I. Borbáth, et al, Top. Catal. (2021). doi:10.1007/s11244-021-01513-1

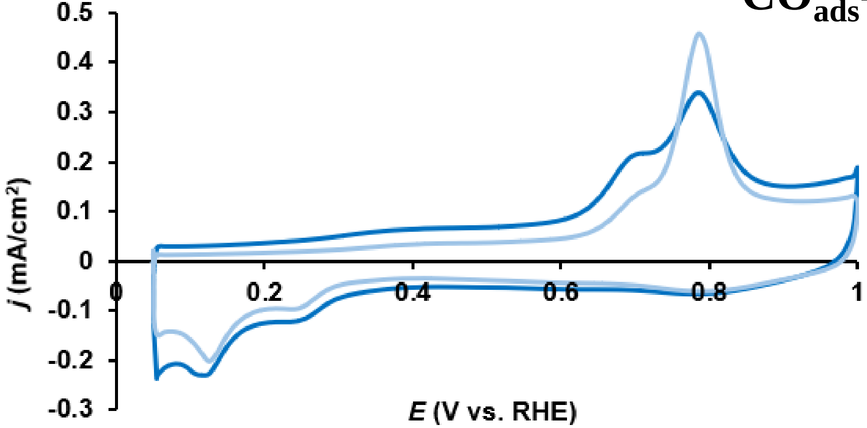
TiO_2-C composites
GO derived carbonaceous material

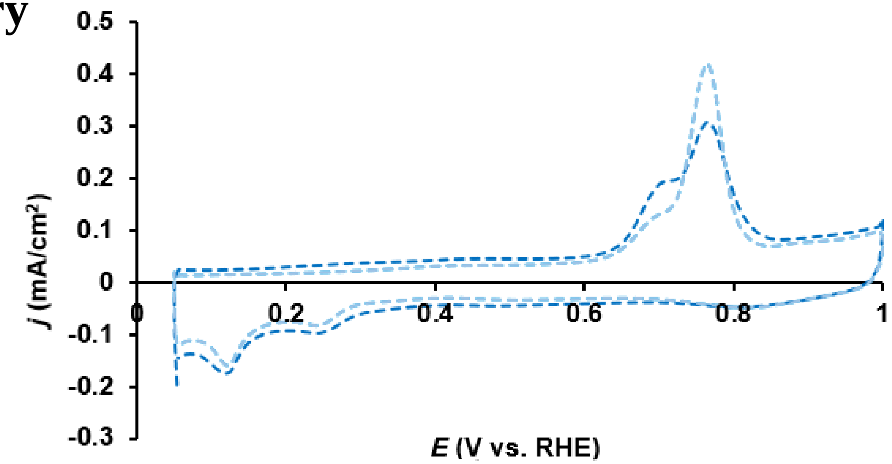
Cyclic voltammetry





CO_{ads}-stripping voltammetry





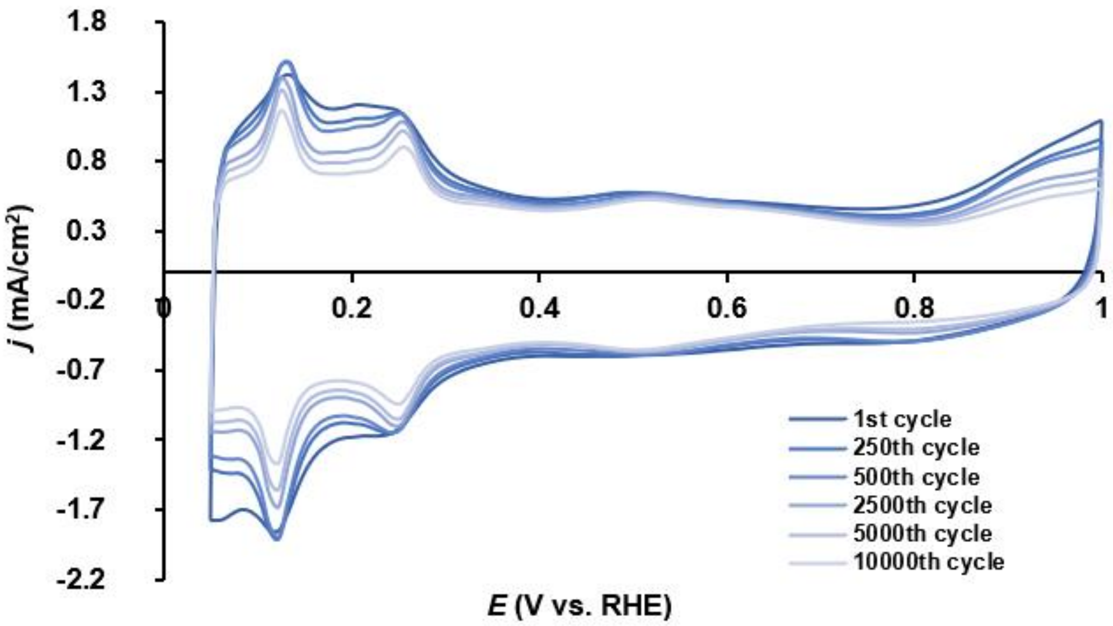
Solid line: before 500-cycle stability test, dashed line: after 500-cycle stability test. Pt/TiBP ( ) and Pt/TiGO ( )

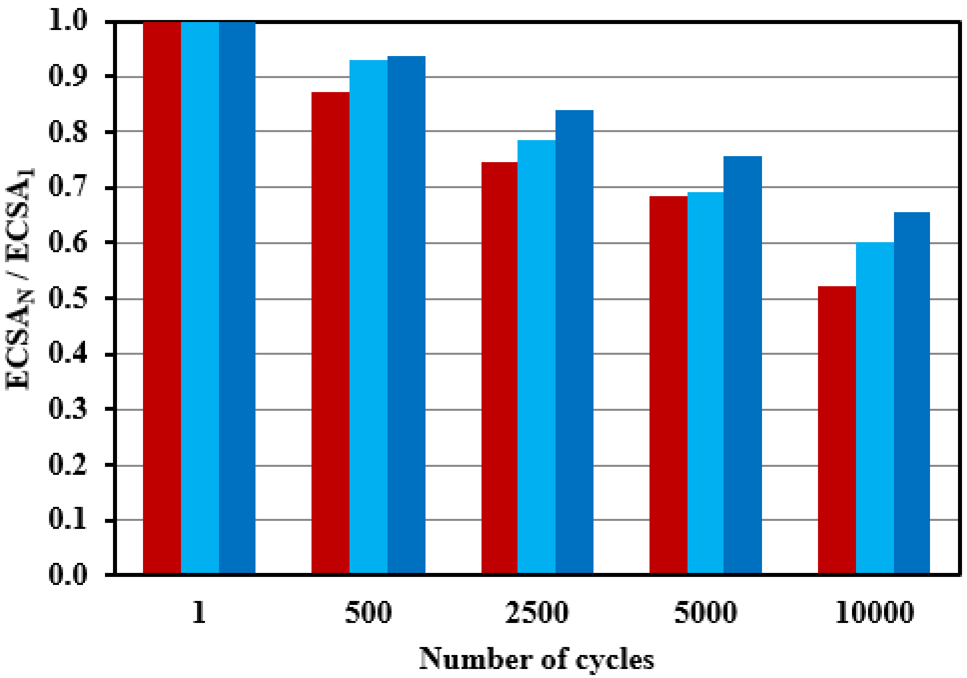
Sample	$E_{CO,max}$, mV	$ECSA_1$, m^2/g_{Pt}	$\Delta ECSA_{500}$, %	$\Delta ECSA_{10,000}$, %
Pt/TiGO	775 (sh: 705)	82.9	6.4	34.3
Pt/TiBP	775 (sh: 705)	82.0	7.0	39.9
Pt/C	795	94.5	12.7	47.8

Ref. I. Ayyubov, I. Borbáth, et al, Top. Catal. (2021) . doi:10.1007/s11244-021-01513-1

TiO_2-C composites
GO derived carbonaceous material

Electrochemical long-term stability test





Cyclic voltammograms of the **Pt/TiGO** catalyst recorded in 0.5 M H_2SO_4 after 1, 250, 500, 2500, 5000, and 10000 cycles of the stability test at 100 mV/s sweep rate.

Electrochemically active Pt surface area measured after N cycles normalized to ECSA measured in the 1st cycle ($ECSA_N/ECSA_1$):

Pt/TiBP ( ), Pt/TiGO ( ) and Pt/C ( )

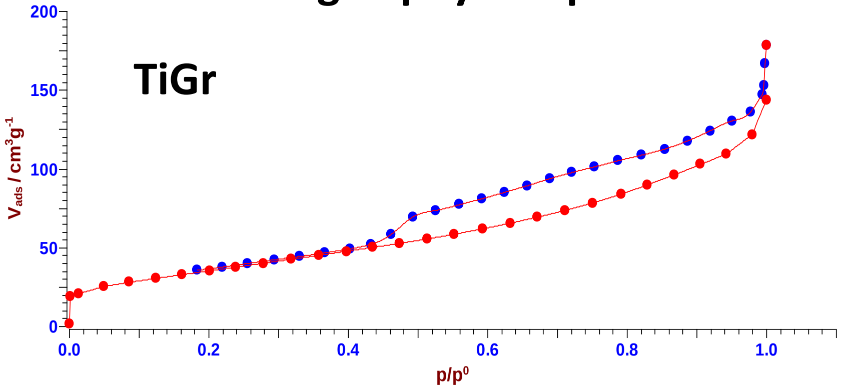
Increased long term stability: Pt/TiGO > Pt/TiBP > Pt/C

Ref. I. Ayyubov, I. Borbáth, et al, Top. Catal. (2021). doi:10.1007/s11244-021-01513-1

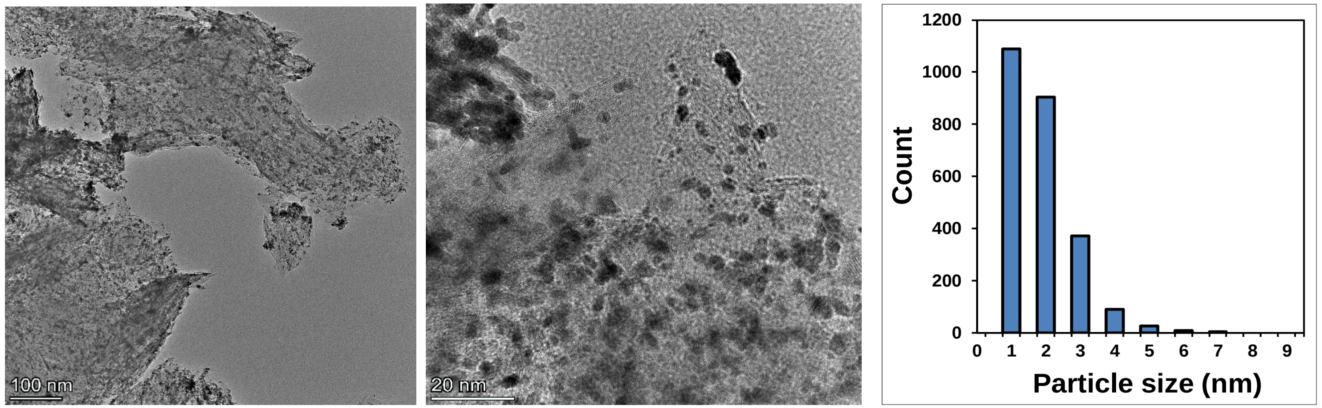
TiO_2-C composites
Multilayer graphene carbonaceous material

Preparation: ball-milling method

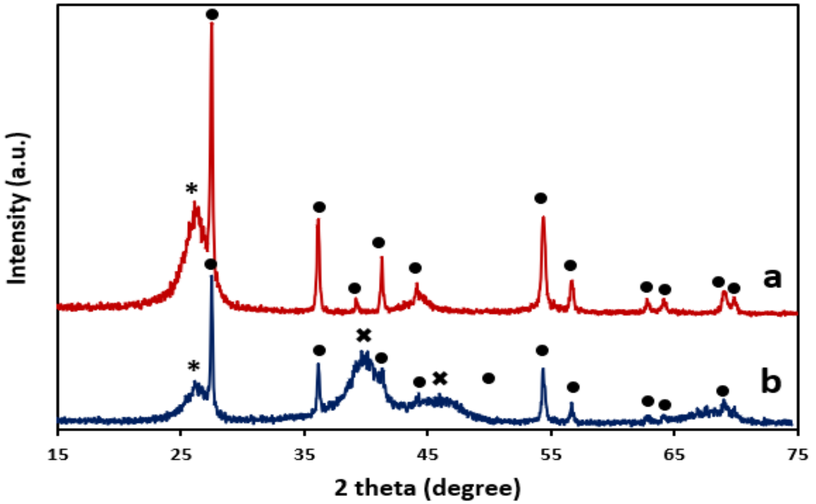
Nitrogen physisorption



TEM



XRD



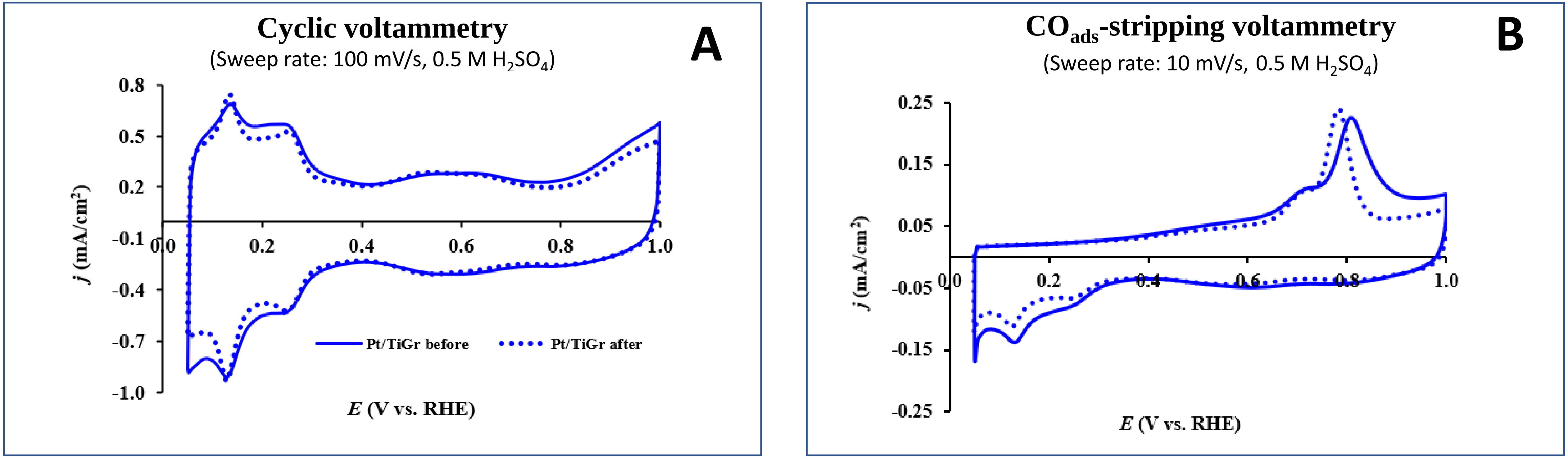
a: TiGr, b: Pt/TiGr, ✱-Carbon, ●-Rutile, ✖-Pt

Sample	XRD parameters				
	2θ (°)	FWHM (°)	D (nm)	d (nm)	n
Graphite	26.39	0.255	44	0.337	131
TiGr	26.12	1.71	5	0.341	15
Pt/TiGr	26.16	1.62	5	0.34	18

Sample	Raman parameters		L_a (nm)
	I_D/I_G	I_{2D}/I_G	
Graphite	0.15	0.55	115
TiGr	1.63	0.41	10.3

Ref. I. Ayyubov, A. Vulcu, et al, React. Kinet. Mech. Catal. 2022, 135, 49–69. doi:10.1007/s11144-021-02138-x

TiO_2-C composites
Multilayer graphene carbonaceous material



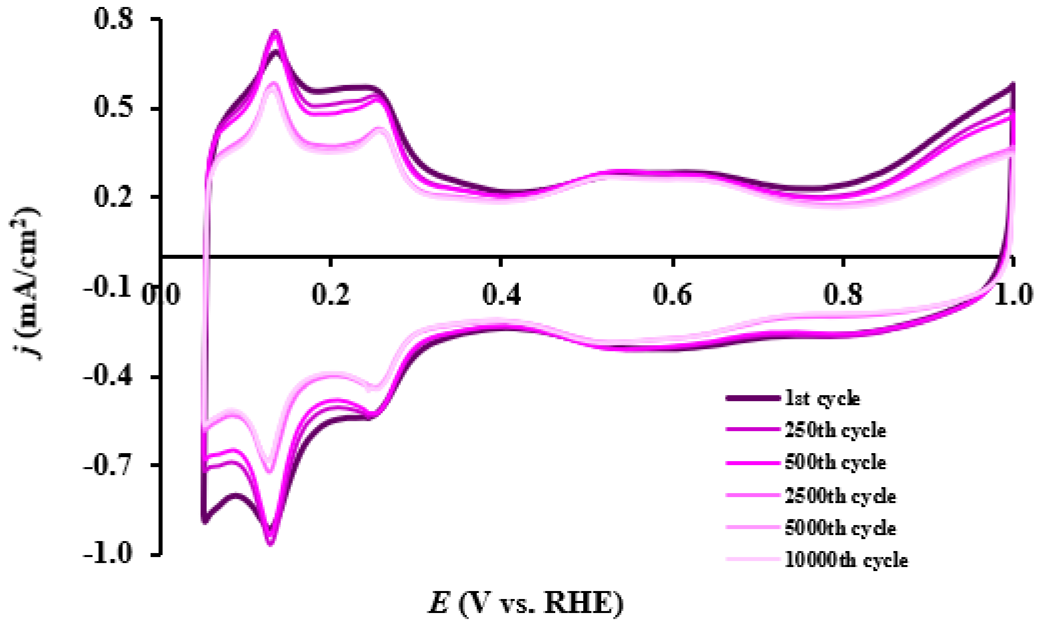
Cyclic voltammograms (A) and CO_{ads} stripping voltammograms (B) of the Pt/TiGr catalyst recorded before (solid line) and after (dotted line) 500-cycle stability test.

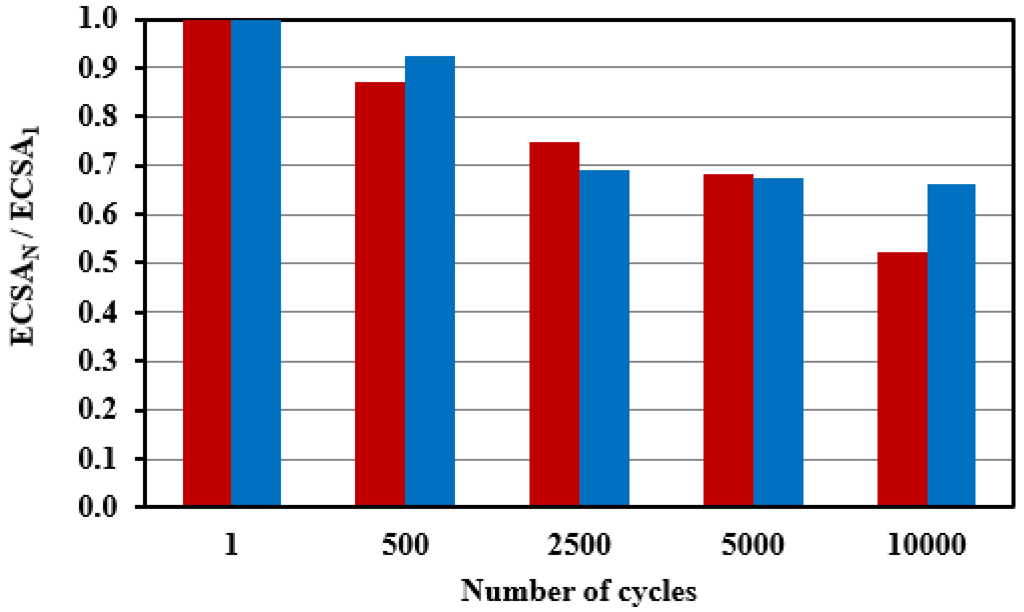
Sample	$E_{CO,max}$, mV	$ECSA_1$, m^2/g_{Pt}	$\Delta ECSA_{500}$, %	$\Delta ECSA_{10,000}$, %
Pt/TiGr	805 (sh: 705)	40.0 ± 2.8	7.6	33.6

Ref. I. Ayyubov, A. Vulcu, et al, React. Kinet. Mech. Catal. 2022, 135, 49–69. doi:10.1007/s11144-021-02138-x

TiO_2-C composites
Multilayer graphene carbonaceous material

Electrochemical long-term stability test





Cyclic voltammograms of the **Pt/TiGr** catalyst recorded in 0.5 M H_2SO_4 after 1, 250, 500, 2500, 5000, and 10000 cycles of the stability test at 100 mV/s sweep rate.

Electrochemically active Pt surface area measured after N cycles normalized to ECSA measured in the 1st cycle ($ECSA_N/ECSA_1$): **Blue: Pt/TiGr, Red: Pt/C**

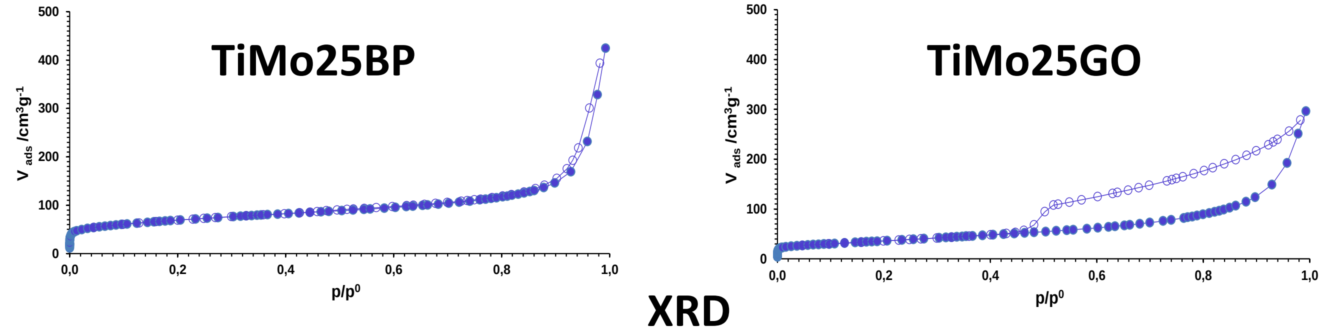
Increased long term stability: Pt/TiGr > Pt/C

Ref. I. Ayyubov, A. Vulcu, et al, React. Kinet. Mech. Catal. 2022, 135, 49–69. doi:10.1007/s11144-021-02138-x

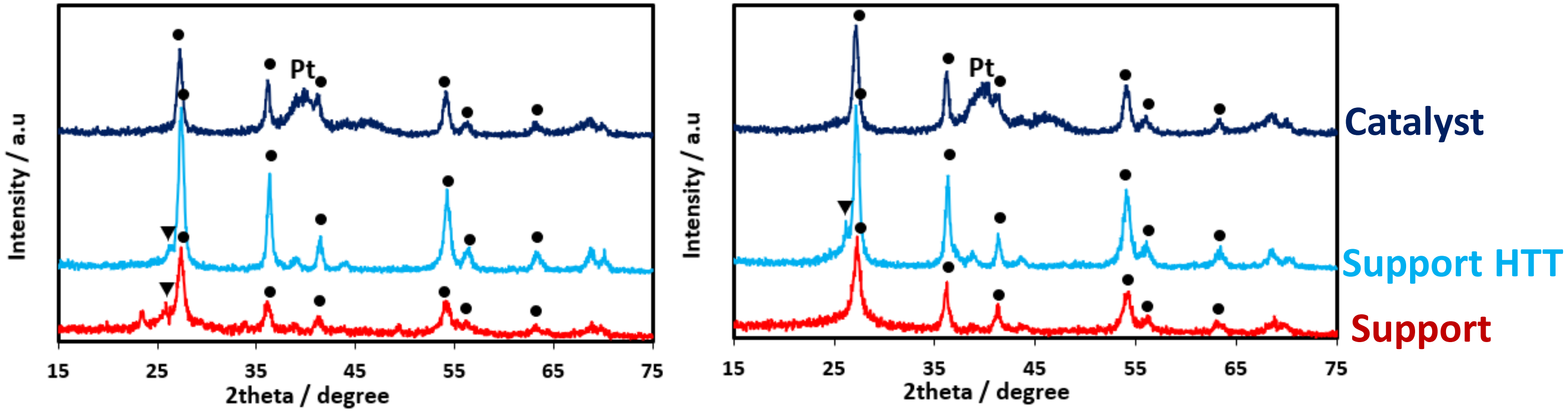
$Ti_{0.8}Mo_{0.2}O_2$-C composites
GO derived carbonaceous material

Preparation: sol-gel method

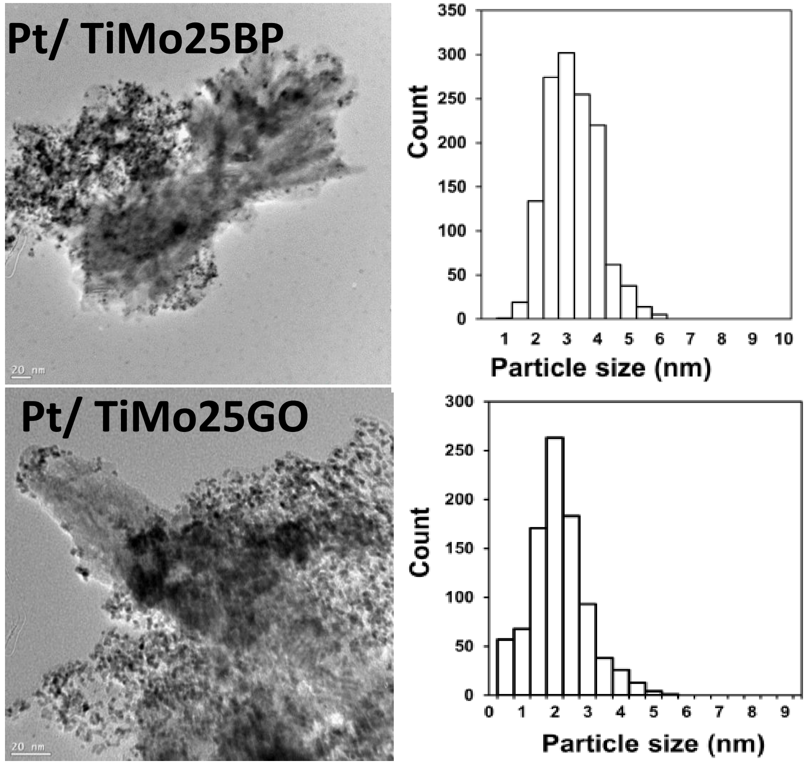
Nitrogen physisorption



XRD



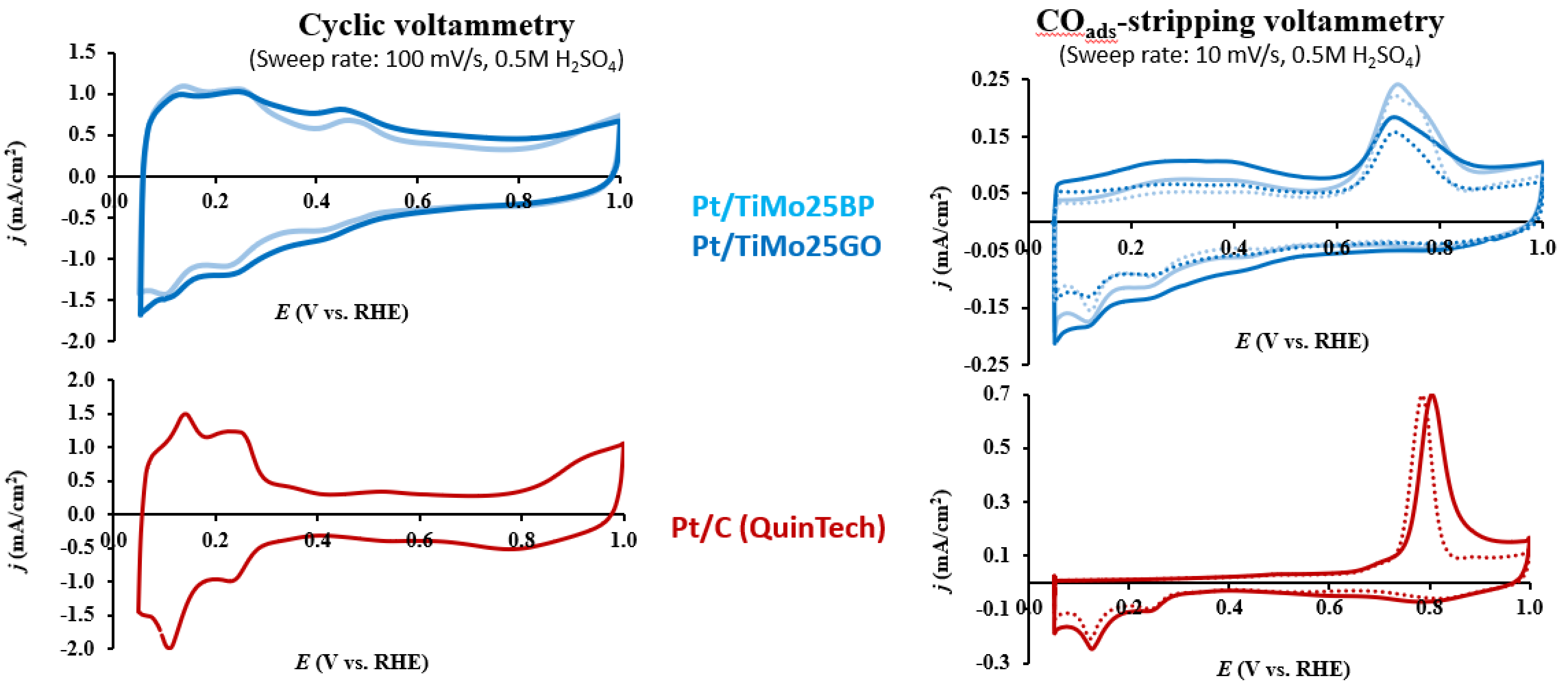
TEM



Sample	Nominal composition	S_{BET}, m^2/g	Pore volume, cm^3/g	Pt size (TEM), nm	Mo subst, (XRD) %
TiMo25BP	$75Ti_{0.8}Mo_{0.2}O_2$-25C	248	0.51	2.9 ± 0.8	18
TiMo25GO	$75Ti_{0.8}Mo_{0.2}O_2$-25C	130	0.39	2.4 ± 0.9	23
Pt/TiMo25BP	$20Pt/75Ti_{0.8}Mo_{0.2}O_2$-25C	-	-	2.9 ± 0.8	18
Pt/TiMo25GO	$20Pt/75Ti_{0.8}Mo_{0.2}O_2$-25C	-	-	2.4 ± 0.9	23

Ref. I. Borbáth, E. Tálas, et al, Appl. Catal. A, Gen. 2021, 620, 118155. https://doi.org/10.1016/j.apcata.2021.118155

$Ti_{0.8}Mo_{0.2}O_2$-C composites
GO derived carbonaceous material

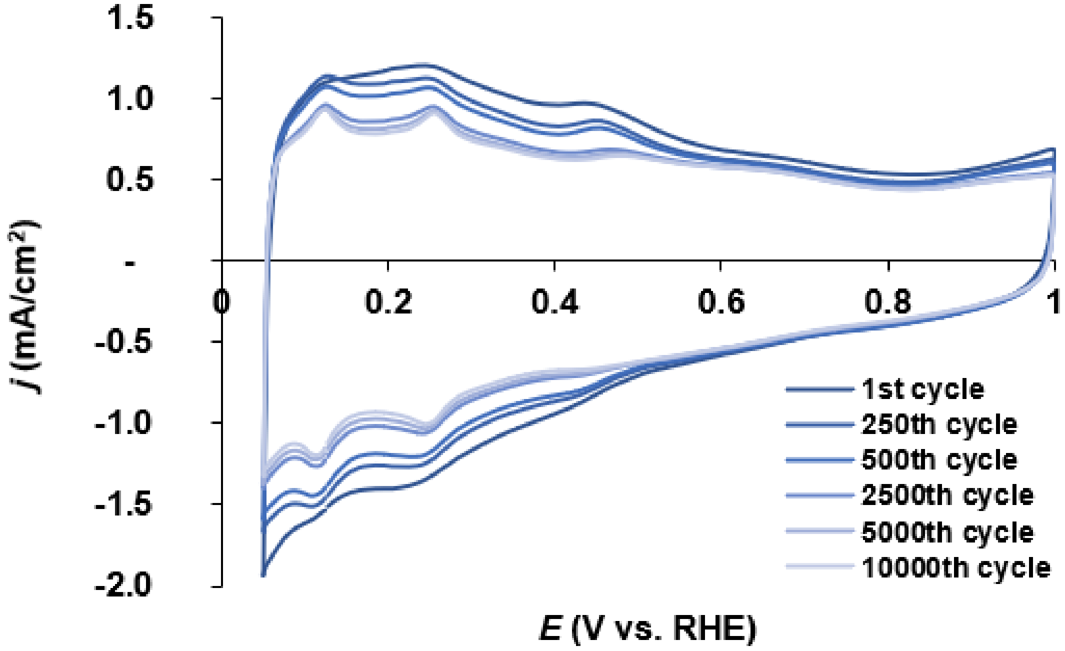


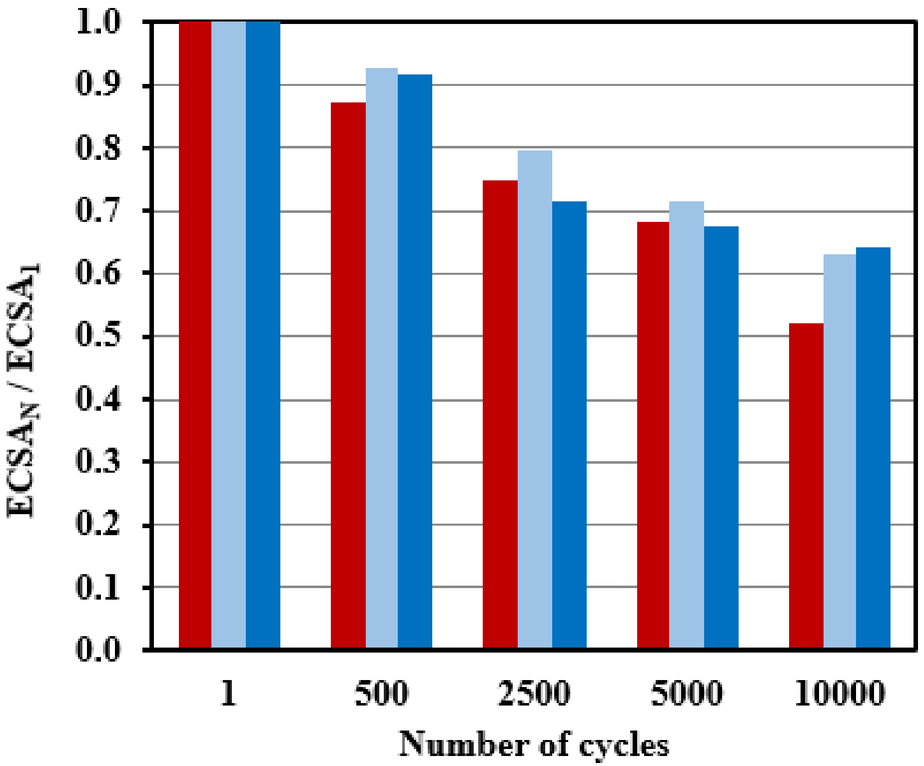
Cyclic voltammograms of fresh catalysts (left column) and CO_{ads} stripping voltammograms (right column) recorded before (solid line) and after (dotted line) 500-cycle stability test.

Increased CO tolerance: Pt/TiMo25GO, Pt/ TiMo25BP > Pt/C

Ref. I. Borbáth, E. Tálas, et al, Appl. Catal. A, Gen. 2021, 620, 118155. https://doi.org/10.1016/j.apcata.2021.118155

$Ti_{0.8}Mo_{0.2}O_2$-C composites
GO derived carbonaceous material





Cyclic voltammograms of the **Pt/TiMo25GO** catalyst recorded in 0.5 M H_2SO_4 after 1, 250, 500, 2500, 5000, and 10000 cycles of the stability test at 100 mV/s sweep rate.

Electrochemically active Pt surface area measured after N cycles normalized to ECSA measured in the 1st cycle ($ECSA_N/ECSA_1$)

Pt/C (QuinTech), Pt/TiMo25BP, Pt/TiMo25GO

Long term stability: Pt/TiMo25GO ~ Pt/TiMo25BP > Pt/C

Ref. I. Borbáth, E. Tálas, et al, Appl. Catal. A, Gen. 2021, 620, 118155. https://doi.org/10.1016/j.apcata.2021.118155

Future plans

Graphite Oxide (GO) based electrocatalysts

- Preparation
- Physicochemical characterization
- Electrochemical characterization

Multilayer Graphene based electrocatalysts

- Preparation
- Physicochemical characterization
- Electrochemical characterization

Graphene Nanoplatelets (GNP) based electrocatalysts

- Preparation
- Physicochemical characterization
- Electrochemical characterization

Nitrogen-doped Graphite Oxide (NGO) based electrocatalysts

- Preparation
- Physicochemical characterization
- Electrochemical characterization

Summary

TiO_2 containing samples demonstrated higher stability compared to the commercially available Pt/C catalyst

Stability of the GO-derived catalysts is higher than that of Black Pearls carbon-containing ones and commercial Pt/C catalyst

Electrochemically active surface area of the catalysts synthesized by sol-gel method is much higher than that of the catalyst synthesized by ball-milling technique

Mo-containing samples showed enhanced CO tolerance

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Zoltán May (RCNS, ELKH) - ICP-OES measurements
Ildikó Turi (RCNS, ELKH) – technical assistence

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SZÉCHENYI 2020

Magyarország Kormánya

Európai Unió
Európai Regionális Fejlesztési Alap

BEFEKTETÉS A JÖVŐBE

Thank you for your kind attention!

A1. XPS, ICP results (Mo-containing samples)

Sample	XPS			ICP		
	Pt, wt.%	(Ti+Mo+O)/C, wt.%/wt.%	Ti/Mo, at%/at%	Pt, wt.%	$Ti_{(1-x)}Mo_xO_2$/C, wt%/wt%	Ti/Mo, mol/mol
Pt/TiMo25GO	39.1	54.9/45.1	2.5	19.0	70.6/29.4	3.6/1
Pt/TiMo25BP	41.5	54.8/45.2	3.2	20.0	65.0/35.0	5.3/1

A2. Electrochemically active surface area calculation

$\textbf{ECSA}_{Hupd}$ (cm^2) = QoxHupd(μC) / 210 (μC/cm^2),

Q_{oxHupd} = charge accompanies oxidation of underpotentially deposited hydrogen,
210 μC = charge necessary to oxidize monolayer of H atoms over 1 cm^2 Pt surface.

Δ ECSA= $\{1-(ECSA_{500}/ECSA_1)\}\times 100\%$ - ECSA drop after stability test,
i.e., indicator of the stability