Supporting Information

A laboratory-based multifunctional near ambient pressure XPS system for electrochemical, catalytic and cryogenic studies

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Section A: Detailed manipulator description

All manipulators (VAb Vakuum-Anlagenbau GmbH, 25337, Elmshorn, Germany) consist of a sample stage (described in the main text) which is connected via a tube including the respective supply lines (e.g., electric wires, cooling pipes, etc.). The corresponding connections are indexed and descripted in figure S1. The moveable part of the gas-solid manipulator (Fig. S1, a) is operated automatically by software-controllable motors and can be adjusted in x-, y-, z-direction and tilted in polar angle, whereas the EC and cryo manipulators are operated manually. To ensure sufficient lateral movement, the supply-line tube is covered by a UHV bellow with long z-travel range.



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Figure S1. Overview of the three different manipulators for a) heterogeneous (electro)catalysis for solid state/gas phase reactions, b) energy-relevant solid/liquid interface electrochemistry and c) atmospheric/ice chemistry at cryogenic temperatures. The different features are indexed with: (1) 2 K-Type connectors, (2) electrochemical connections, (3) Pt-100 and resistive heater connectors and (4) cooling ports for cold gas or liquid cooling.

Section B: Details of XPS analysis and fitting parameters

All illustrated XP-spectra were recorded applying a pass energy of 50 eV and a step size of 0.1 eV. The dwell time for each adjusted step was set to 0.1 s.

Table S1. Fitting parameters for the fits of the Pt 4f and O 1s regions shown in Fig. 7. A Shirley type background was utilized for all regions.

Potential / V _{RHE}	Binding energy [FWHM] / eV F							
	Pt 4f _{7/2} region		Pt 4f _{5/2} region		O 1s region			
_	Pt^0	Pt^{δ^+}	Pt^0	Pt^{δ^+}	GPW	LPW		
0	71.2*	n.a.	74.5*	n.a.	536.0	533.7	Fig. 7	
	[0.9]		[0.9]		[0.9]	[2.0]	A/B	
1.2	71.2*	72.6	74.5	75.9	535.3	532.9	Fig. 7	
	[1.0]	[1.4]	[1.0]	[1.4]	[0.9]	[2.0]	A/B	
Peak	LA(1.2,85,70)	GL(30)	LA(1.2,85,70)	GL(30)	GL(30)	GL(30)		
shape								

*As an asymmetric peak shape was utilized to fit the metallic component it should be noted that the binding energy position is related to the peak maximum of the fitted species.

Table S2. Fitting parameters for the fits of the O 1s and C 1s regions shown in Fig. 9. A Shirley type background was utilized for all regions.

CO ₂	Binding	Comments		
adsorption				
	O 1s region		C 1s	
			region	
	CO_2 (ad)	$H_2O(s)$	CO_2 (ad)	
	539.0	536.9	295.2	Before
Before CO ₂	[1.6]	[2.0]	[1.7]	calibration
exposure	536.4	534.5	292.8	After
	[1.4]	[2.0]	[1.7]	calibration
	541.9	539.8	298.2	Before
After CO ₂	[1.6]	[2.1]	[1.6]	calibration
exposure	536.4	534.4	292.8	After
	[1.6]	[2.1]	[1.6]	calibration
Peak shape	GL(30)	GL(30)	GL(30)	

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