

Supplemental Information for “Electrochemical Capacitance of CO-terminated Pt(111) is Dominated by CO-Solvent Gap”

Ravishankar Sundararaman,^{*,†} Marta C. Figueiredo,[‡] Marc T. M. Koper,[¶] and Kathleen A. Schwarz^{*,§}

[†]Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12189, USA

[‡]University of Copenhagen Department of Chemistry Nano-Science Center Universitetsparken, 5 2100 Copenhagen, Denmark

[¶]Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

[§]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Received October 16, 2017; E-mail: sundar@rpi.edu; kas4@nist.gov

The double layer capacitance for Pt(111) and for Pt(111)/CO_{ads} was extracted by from the cyclic voltammograms at different scan rates. Before each scan rate experiment the uncompensated resistance was determined by potentiostatic electrochemical impedance spectroscopy for Pt(111) at 0.4 V (potential within the double layer region). The frequency range was usually between 20 kHz and 10 Hz. In the Nyquist plot, a line is fitted through the data points corresponding to higher frequencies and the intercept with the real axis is obtained. To avoid overcompensation and instabilities in the potentiostat control, 85% of this value is used in the potentiostat’s IR compensation function.

Figure S1 A and B show the positive sweep of the cyclic voltammograms obtained at different supporting electrolyte concentrations. The presence of the characteristic well-defined features of Pt(111) (Figure S1 A) shows the cleanliness and high order of the surface.

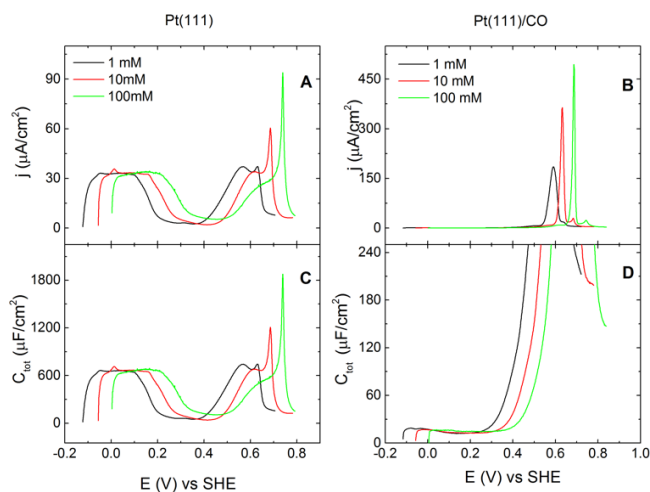


Figure S1. Positive going sweeps for the cyclic voltammograms after potential correction of A) Pt(111) and B) Pt(111)/CO at 0.05 Vs^{-1} and 0.02 Vs^{-1} , respectively; Pseudo capacitance curves calculated from the CVs for C) Pt(111) and D) Pt(111)/CO ($C = j/v$, $v = 0.05 \text{ Vs}^{-1}$ for Pt(111) and 0.02 Vs^{-1} for Pt(111)/CO) at different electrolyte concentrations.

It is known that the experimental determination of the pure double layer capacitance (C_{dl}) of Pt is difficult due to adsorption processes.^{1–3} Even with experiments in the absence of specifically adsorbed anions, such as perchlorates, H and OH adsorption will lead to much larger capacitance values than the typical ones considered for double layer.

García-Araez et al.¹ described a thermodynamic model for the determination of the C_{dl} by using total charge densities versus potential curves in solutions with and without chloride based on the fact that the total charge of Pt(111) in solutions containing Cl^- become pH independent at potentials where H and OH adsorption are suppressed due to the adsorption of Cl^- .

For this study, the pseudo capacitance values (C_{tot}) for Pt(111) and Pt(111)/CO were extracted by measuring the current density at 0.4 V at different scan rates (Table 1 in the manuscript), and also by direct analysis of the cyclic voltammograms (Figure S1). The obtained values are in good agreement with previous reports both theoretical predictions⁴ as well as experimental results.^{1,2,5}

For the clean Pt(111) electrode, both the pseudo capacitance as the double layer capacitance increase with the ionic strength of the solutions. This behavior shows the effect of the Gouy-Chapman diffuse layer on the overall capacitance. However, when the surface is covered by adsorbed CO, the double layer capacitance decreases drastically to $11 \mu\text{F}/\text{cm}^2$ and becomes independent of the electrolyte concentration.

References

- (1) García-Araez, N.; Climent, V.; Herrero, E.; Feliu, J. M.; Lipkowsky, J., Thermodynamic Approach to the Double Layer Capacity of a Pt(111) Electrode in Perchloric Acid Solutions. *Electrochim. Acta* **2006**, *51*, 3787-3793.
- (2) Pajkossy, T.; Kolb, D. M., Double Layer Capacitance of Pt(111) Single Crystal Electrodes. *Electrochim. Acta* **2001**, *46*, 3063-3071.
- (3) Climent, V.; García-Araez, N.; Herrero, E.; Feliu, J., Potential of Zero Total Charge of Platinum Single Crystals: A Local Approach to Stepped Surfaces Vicinal to Pt(111). *Russ. J. Electrochem.* **2006**, *42*, 1145-1160.
- (4) Rossmesl, J.; Skúlason, E.; Björketun, E.; Tripkovic, V.; Nørskov, J. K., Modeling the Electrified Solid-Liquid Interface. *Chem. Phys. Lett.* **2008**, *466*, 68-71.
- (5) Cuesta, A., Measurement of the Surface Charge Density of CO-saturated Pt(111) Electrodes as a Function of Potential: the Potential of Zero Charge of Pt(111). *Surf. Sci.* **2004**, *572*, 11-22.