Supporting Information

How the ionic liquid $[C_2C_1Im][OTf]$ affects the stability of Pt(111) during potential cycling

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1. Dissolution of Pt(111) and Pt_{poly}

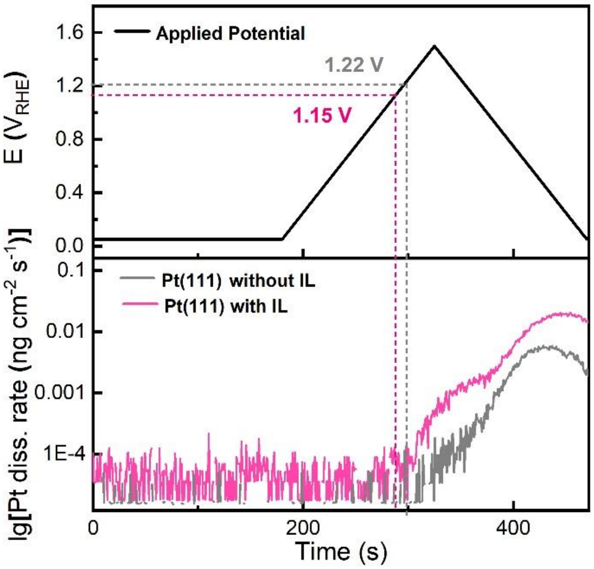

Figure S1: Semi-logarithmic plot of the Pt(111) dissolution in absence and in presence of 10 mM [C_2C_1Im][OTf] measured by online ICP-MS; applied electrochemical potential window 0.05-1.5 V_{RHE}, scan rate 10 mV·s^{-1}. The dissolution onset potential (vertical dash lines) was determined at a signal/noise ratio of 3 (S/N=3).

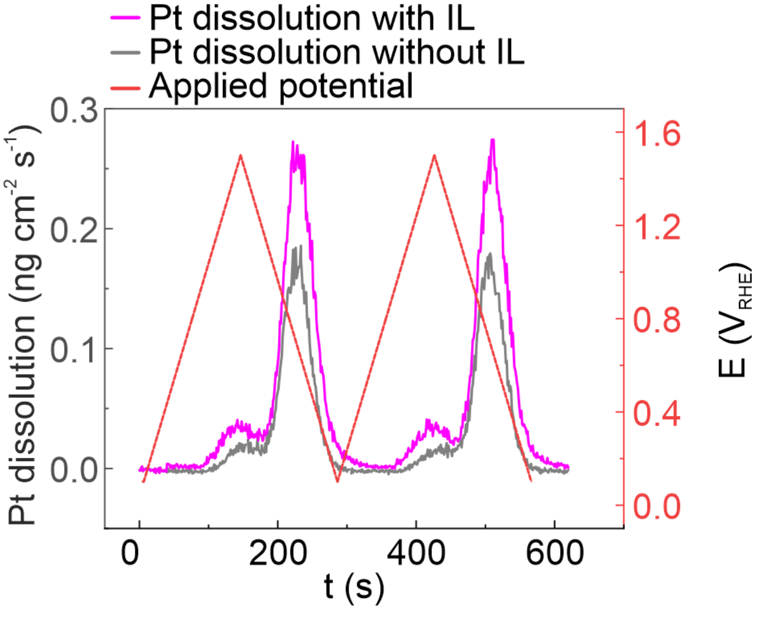

Figure S2: Online dissolution profiles for two consecutive CVs from polycrystalline Pt in 0.1 M $HClO_4$ in the absence and presence of 10 mM [C_2C_1Im][OTf]; applied electrochemical potential window 0.05 - 1.5 V_{RHE}, scan rate 10 mV·s^{-1}.

2. Pt(111) surface cleaning procedure

To understand the influence of residual ionic liquid (IL) on the characterization CVs, we performed a series of experiments. We prepared two CV cells, one with 0.1 M $HClO_4$ (characterization cell) and one with 1 M [C_2C_1Im][OTf] (exposure cell). First, we characterized the freshly prepared Pt(111) crystal in 0.1 M $HClO_4$. Next, we transferred the crystal to the exposure cell. We brought the crystal surface into contact with the solution for 30 seconds applying 0.05 V_{RHE} to adsorb IL, potential contaminations, and decomposition products. Afterwards, we rinsed the crystal surface with ultrapure water and performed a characterization CV from 0.05 to 0.9 V_{RHE} (50 $mV\cdot s^{-1}$) in the characterization cell. Next, we applied a reductive cleaning procedure of 16 cycles between 0.05 and -1 V_{RHE} with 50 $mV\cdot s^{-1}$ to remove the adsorbates. We purged the solution for 5 minutes with N_2 to remove residual hydrogen from the solution. Then we characterized the crystal surface once again. To see, if we can further remove potential adsorbates, we performed additional 16 hydrogen evolution reaction (HER) cycles, purged with N_2, and characterized the surface again using CV. Finally, we kept the crystal for one hour in contact with the solution of the characterization cell at 0.05 V_{RHE} and measured afterwards a characterization CV to find out whether potential residual adsorbates detach from the surface over time. The resulting voltammograms are shown in Figure S3. The freshly prepared Pt(111) surface shows the hydrogen adsorption/desorption region between 0.05 and 0.3 V_{RHE}, the characteristic butterfly feature at 0.8 V_{RHE} and the double-layer region in between. After the Pt surface was in contact with the IL containing solution, the hydrogen adsorption/desorption region and especially the butterfly region decrease drastically in charge and the peak at 0.8 V_{RHE} becomes very blunt, which we assign to blocking by adsorbates. After 16 cycles of HER, the hydrogen adsorption/desorption region and the butterfly peak are both recovered. Increased amount of HER cycling will not further increase the butterfly peak intensity. Also holding the crystal at 0.05 V_{RHE} in contact with the solution for one hour will not change the surface constitution. We conclude that a treatment of 16 cycles between 0.05 and -1.0 V_{RHE} is sufficient to clean the surface resulting in well-ordered Pt(111) with only traces of adsorbates.

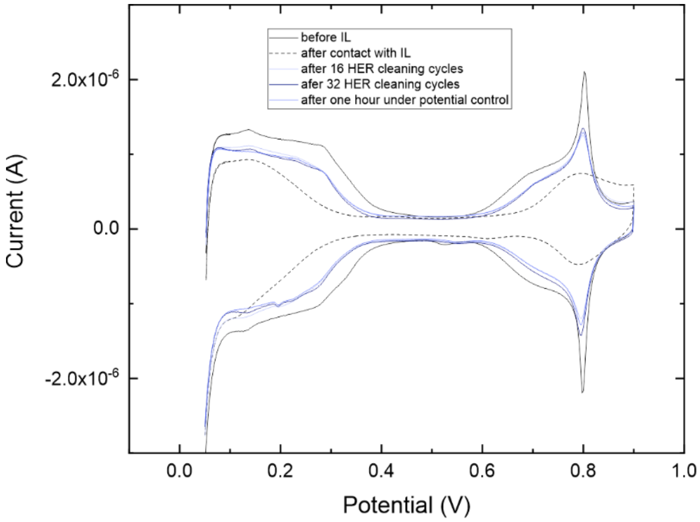

Figure S3: CVs of Pt(111) in 0.1 M $HClO_4$ between 0.05 and 0.9 V_{RHE} after different treatment. Scanrate was 50 $mV\cdot s^{-1}$.

3. Nanoisland size distribution for EC-STM images, 10 – 40 ORCs

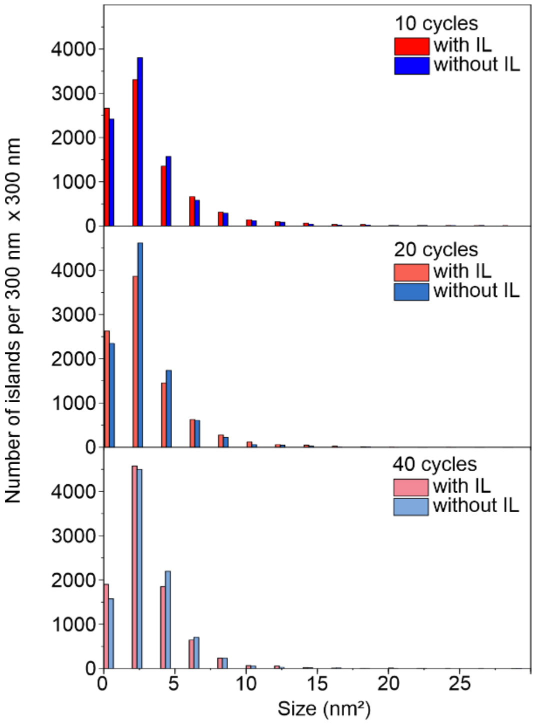

Figure S4: Size distribution histogram of nanoislands in EC-STM images from Figure 4.

The STM images in Figure 4 were analyzed using the same approach as described for Figure 6 (analysis of STM images from Figure 5). Consistent with those results, no substantial differences were observed between the presence and absence of the ionic liquid. Note that the larger scan area of the 300 × 300 nm² images in Figure 4 provides broader sampling compared to the 100 × 100 nm² images in Figure 5. However, the lower resolution of the former limits the sensitivity for detecting subtle morphological differences.

4. Reference electrode preparation

The experiments with up to 800 cycles were performed in the EC-STM cell. There we used a freshly prepared palladium hydrogen electrode. The potential was recalculated against the RHE. The galvanostatic preparation of the reference electrode was performed following a procedure published by Vasile and Enke.[1] First, the Pd wire was cleaned with ultrapure water. The wire was then flame annealed for approximately 1 minute in the blue flame of a Bunsen burner, after which the wire was cooled in air for 10 minutes, followed by another rinse with ultrapure water. An electrochemical cell was prepared containing 0.1 M $HClO_4$. The electrolyte was purged with N_2 for at least 10 minutes. A freshly prepared RHE was applied as RE, and a Pt wire was used as CE. A Pt wire (0.5 mm diameter) was used to hold and electrically contact the palladium wire. The lower part (3-4 mm) of the Pd wire was immersed into the electrolyte. During the galvanostatic treatment, only the atmosphere of the cell was purged with N_2 and no longer the electrolyte. A cathodic current was applied in six 60 second pulses. Each pulse was followed by a 60 s measurement of the OCP. The currents applied during the pulses were 2x -10 mA, 2x -50 mA and 2x -80 mA. Finally, the OCP was measured for at least 20 minutes to verify the stability of the electrode potential. Long-term stability tests show a stable potential of 55 ± 5 $\mathrm{mV_{RHE}}$ of the as-prepared electrode for at least 12 hours.[1]

[1] Vasile, M. J.; Enke, C. G. The Preparation and Thermodynamic Properties of a Palladium-Hydrogen Electrode. *Journal of The Electrochemical Society* 1965, *112* (8), 865. DOI: 10.1149/1.2423713.