



Supporting Information

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Heat-Assisted Electrodeposition of Platinum in an Ionic Liquid**

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Supporting information

Experimental Section

Chemicals: EMIC was prepared and purified according to the method described in the literature.^[1] The ZnCl₂-EMIC IL was prepared in a glove box filled with dry nitrogen gas by mixing the proper amounts of ZnCl₂ (99.99%, Aldrich) and EMIC in a beaker, followed by heating at 90 °C for 1 h to ensure that the reaction between ZnCl₂ and EMIC was complete. The resulting ionic liquid was colorless. Zn wire (99.999%), anhydrous PtCl₂ (99.9%), PtCl₄ (99.9%), and Pt wire (99.95%) were purchased from Aldrich and used as received.

Electrodissolution of platinum electrode: The electrochemical experiments were performed using an Autolab potentialstat/galvanostat (EcoChemie) controlled with GPEs software in a glove box filled with dry nitrogen gas or an electrochemical cell covered with 99.9% argon gas. A three-electrode electrochemical cell was used for the electrochemical experiments. The reference electrode was a Zn wire immersed in a partitioned fritted glass tube containing pure 50–50 mol% ZnCl₂-EMIC IL. A Pt wire was used as a counter electrode and immersed in a partitioned fritted glass tube containing pure 25–75 mol% ZnCl₂-EMIC IL. Pt⁴⁺ was introduced into the ionic liquid at 100 °C by the electrodisolution of a Pt wire electrode at 1.25 V. The oxidation state of Pt ion was determined in accordance with Faraday's laws of electrolysis. The Pt wire of known weight was anodized in a divided cell under controlled-potential conditions. At the end of each experiment, the electrode was removed from the ionic liquid and cleaned with deionized water (specific resistivity is 18.2 MΩ cm⁻¹) and ethanol solution outside the glove box, dried in an oven, and weighed again.

Electrodeposition of pure Pt and PtZn alloy: Electrochemical studies of Pt ion and electrodeposition experiments were directly conducted in the same electrochemical system used in Pt electrodisolution. An ITO glass slide (5.0 mm × 5.0 mm) was used as the

working electrode and as the electroplated substrate. The ITO glass slide was sonicated in acetone and ethanol solutions for 20 min, sequentially rinsed with deionized water (specific resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$), and dried in an oven before being used as the working electrode. Pt and PtZn alloy were obtained by controlled potential at -0.5 V and -0.8 V , respectively. A JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) with an energy dispersive spectrometer (EDS) was used to examine the surface topography and the elemental compositions of the electrodeposits. The microstructure and the composition of pure Pt and PtZn alloy were also characterized with X-ray diffraction (XRD) ($\text{Cu K}\alpha$ radiation) measurement.

Table s1. Results for the anodization of Pt wires

$\Delta w_{\text{Pt}}^{[a]}$ (g)	$10^4 m_{\text{Pt}}^{[b]}$ (mol)	$Q_{\text{theory}} (n=1)^{[c]}$ (C)	$Q_{\text{exp}}^{[d]}$ (C)	$n^{[e]}$
0.0029	0.15	1.44	5.64	3.93
0.0019	0.10	0.94	3.75	3.99
0.0031	0.16	1.53	6.00	3.91
				Avg: 3.94 ± 0.04

[a] The weight loss of Pt; [b] the number of moles for Pt weight change; [c] the theoretical charges based m_{pt} for $n = 1$; [d] the experimental passage of charges; [e] $n = Q_{\text{exp}}/Q_{\text{theory}}$

Figure s1.

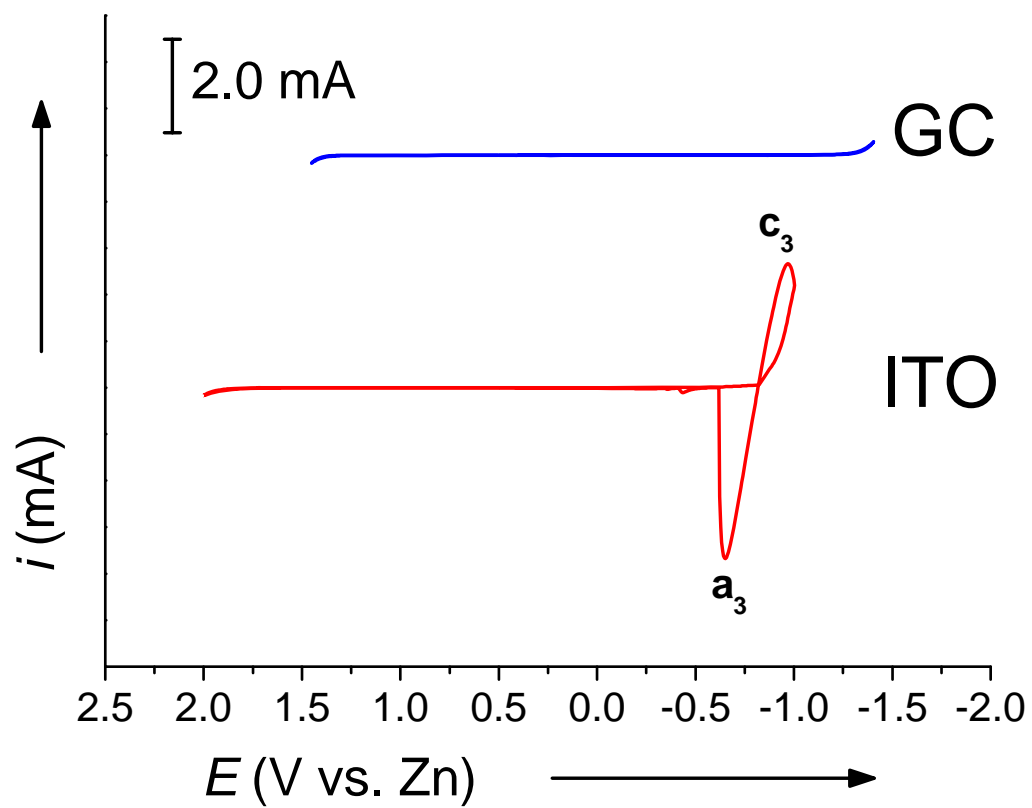


Figure s1. Cyclic voltammograms of 25–75 mol% $ZnCl_2$ -EMIC ionic liquid recorded at GC and ITO electrodes at 100 °C. The scan rate was 50 $mV s^{-1}$.

Figure s2.

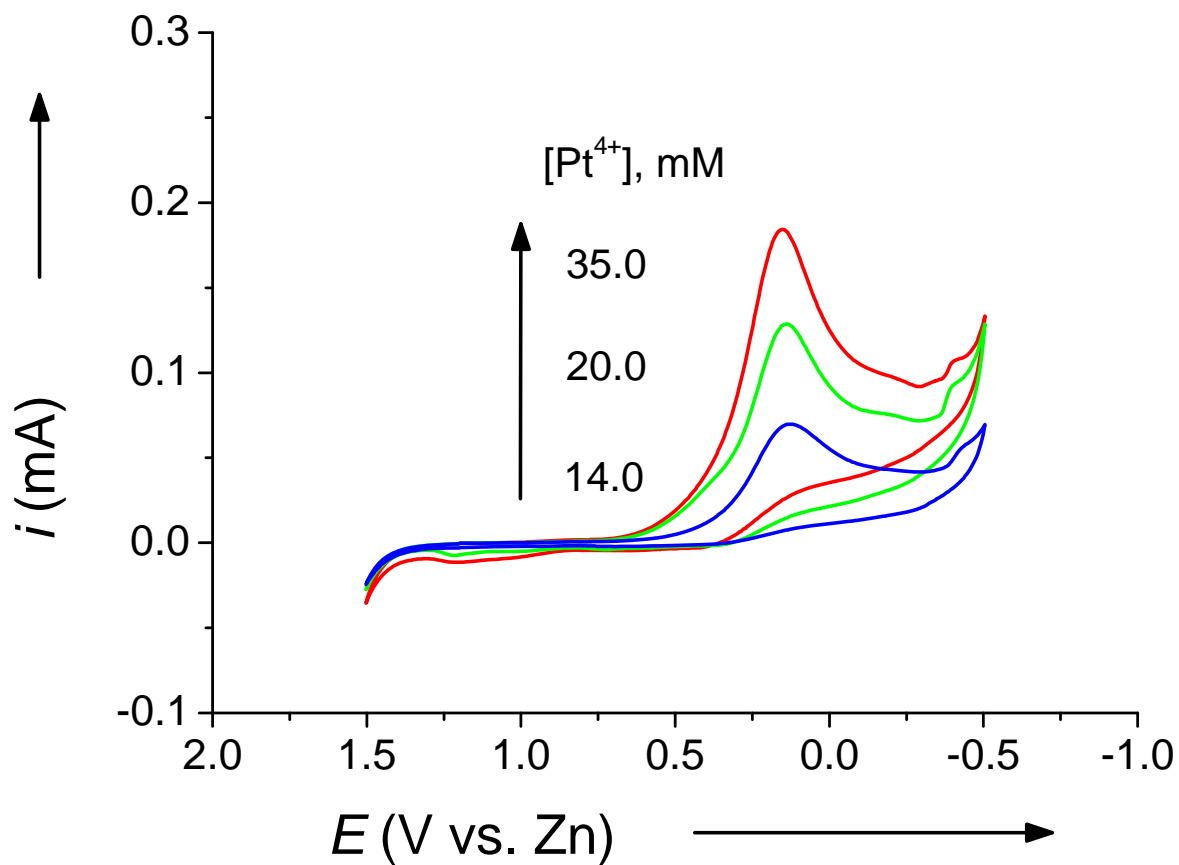


Figure s2. Cyclic voltammograms of 14.0, 20.0 and 35.0 mM Pt^{4+} in basic 25–75 mol% ZnCl_2 -EMIC ionic liquids at the ITO electrode at 100 °C. The scan rate was 50 mV s^{-1} .

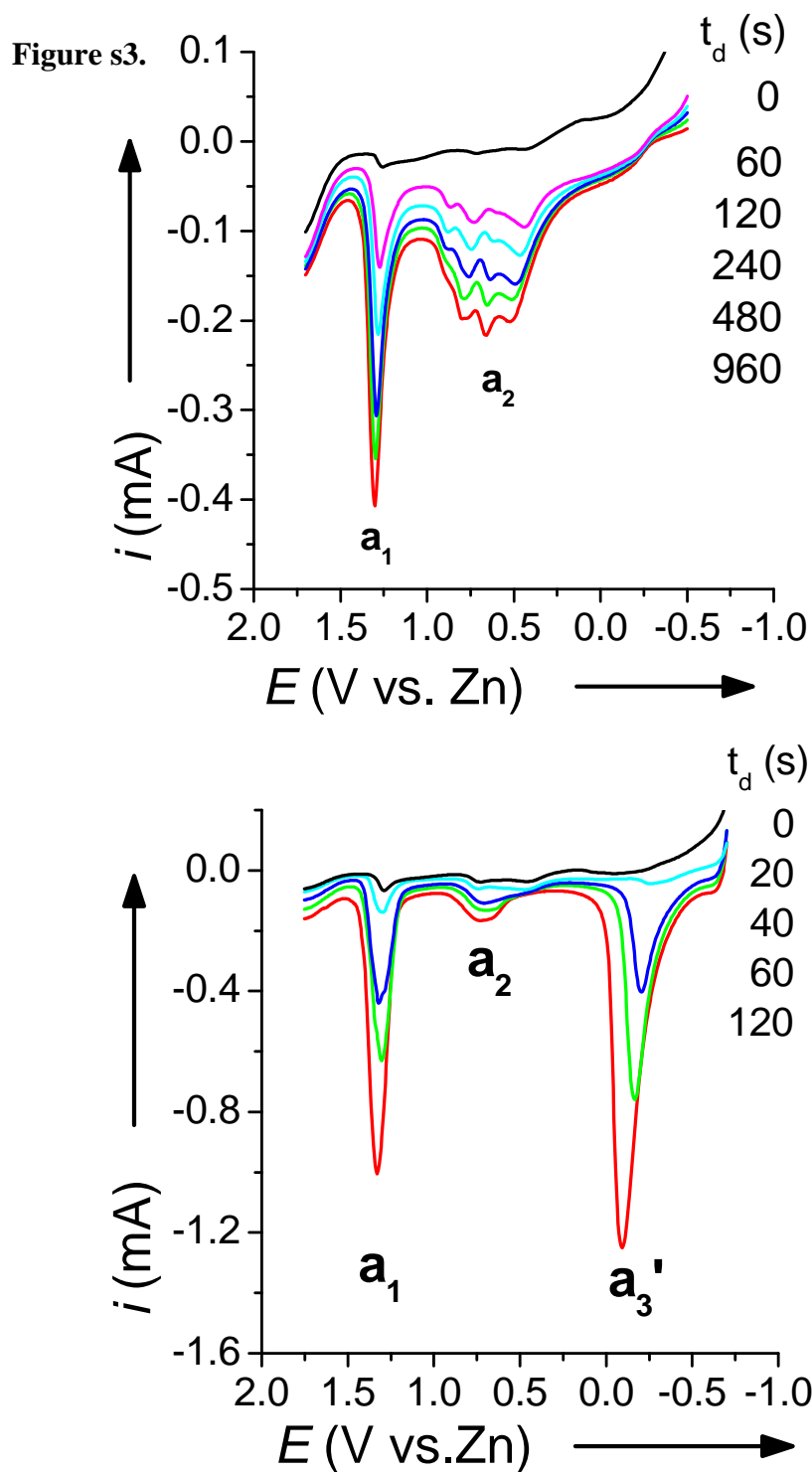


Figure s3. Linear scan stripping voltammograms for the 35.0 mM Pt^{4+} solution at an ITO electrode after cathodic deposition at (upper) -0.5 V and (lower) -0.8 V for different deposition periods. The scan rate was 50 mV s^{-1} .

Figure s4.

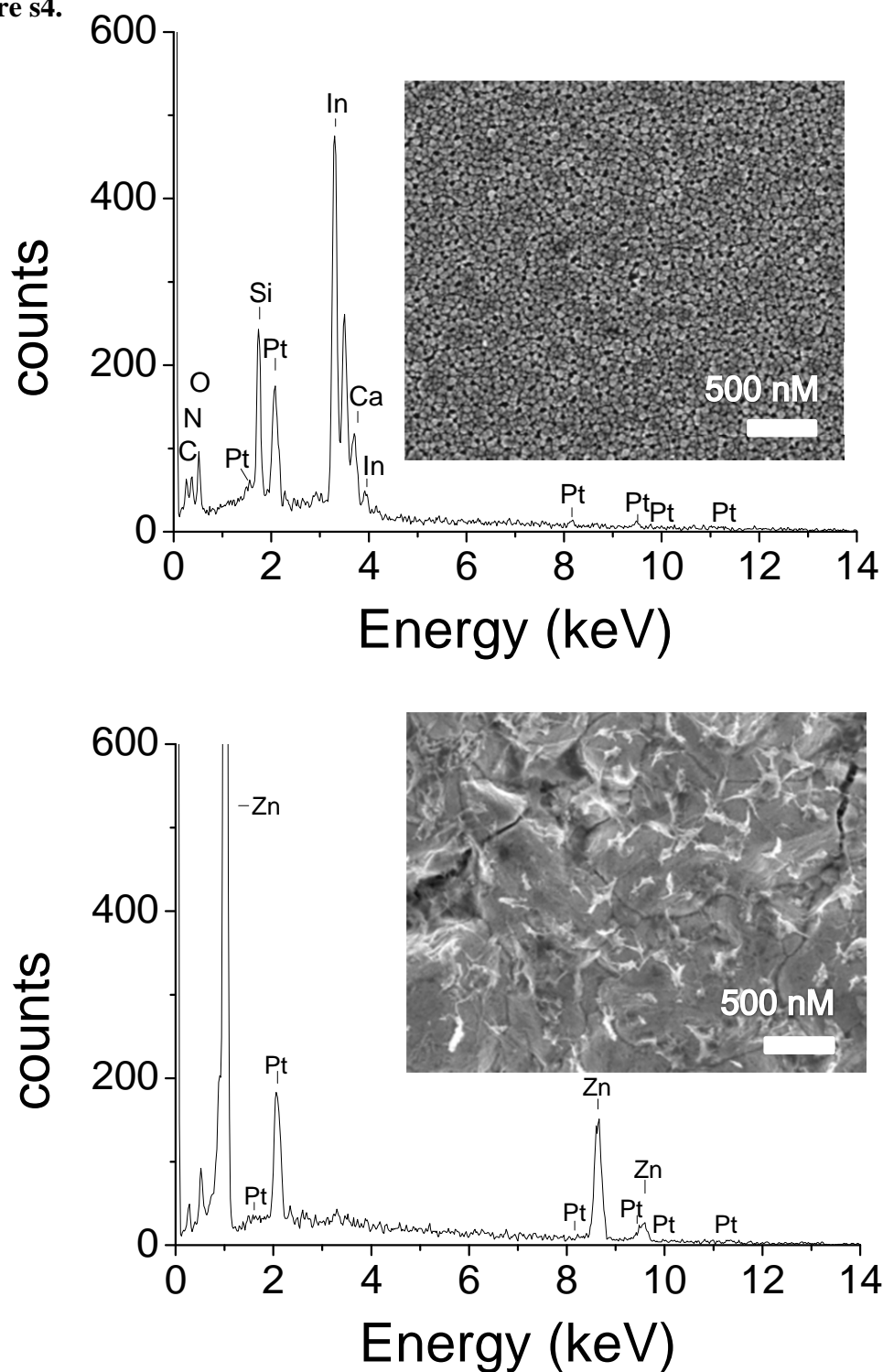


Figure s4. EDS plots of (upper) pure Pt and (lower) Pt-Zn deposits were obtained on ITO substrates with controlled potential at (upper) -0.5 V and (lower) -0.8 V at $T = 100\text{ }^{\circ}\text{C}$ in the 25–75 mol% ZnCl_2 -EMIC ionic liquid containing 35.0 mM Pt^{4+} from electrodisolution of Pt wire. Insets are SEM images of (upper) pure Pt and (lower) Pt-Zn deposits.

Figure s5.

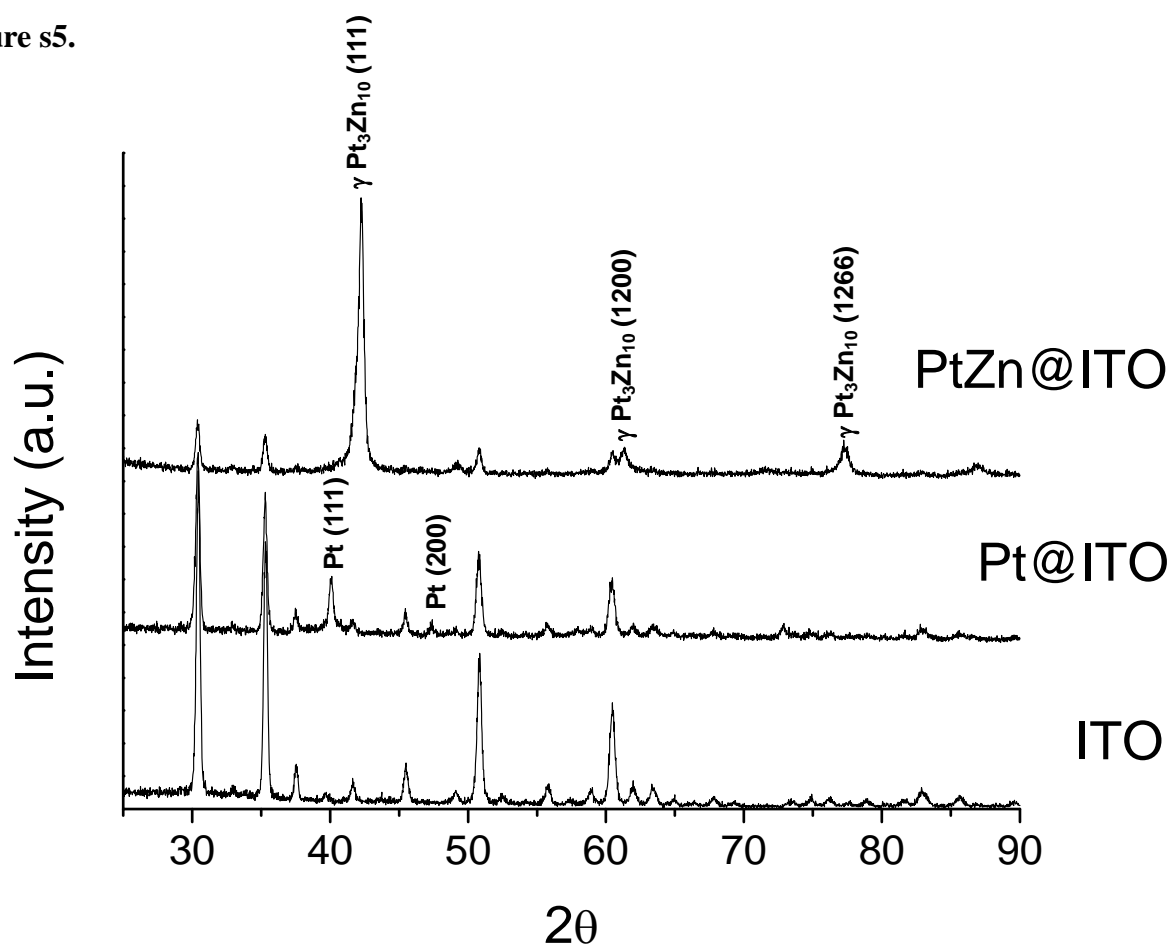


Figure s5. XRD patterns ($\text{Cu K}\alpha$) of Pt and Pt-Zn electrodeposits on ITO substrates and bare ITO substrate. The reflection patterns were assigned in accordance with JCPDS card no. 654913 for $\gamma\text{-Pt}_3\text{Zn}_{10}$ and no. 882343 for Pt.

References

- [1] J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263.