

## Direct methanol oxidation at low overpotentials using Pt nanoparticles electrodeposited at ultrathin conductive RuO<sub>2</sub> nanoskins

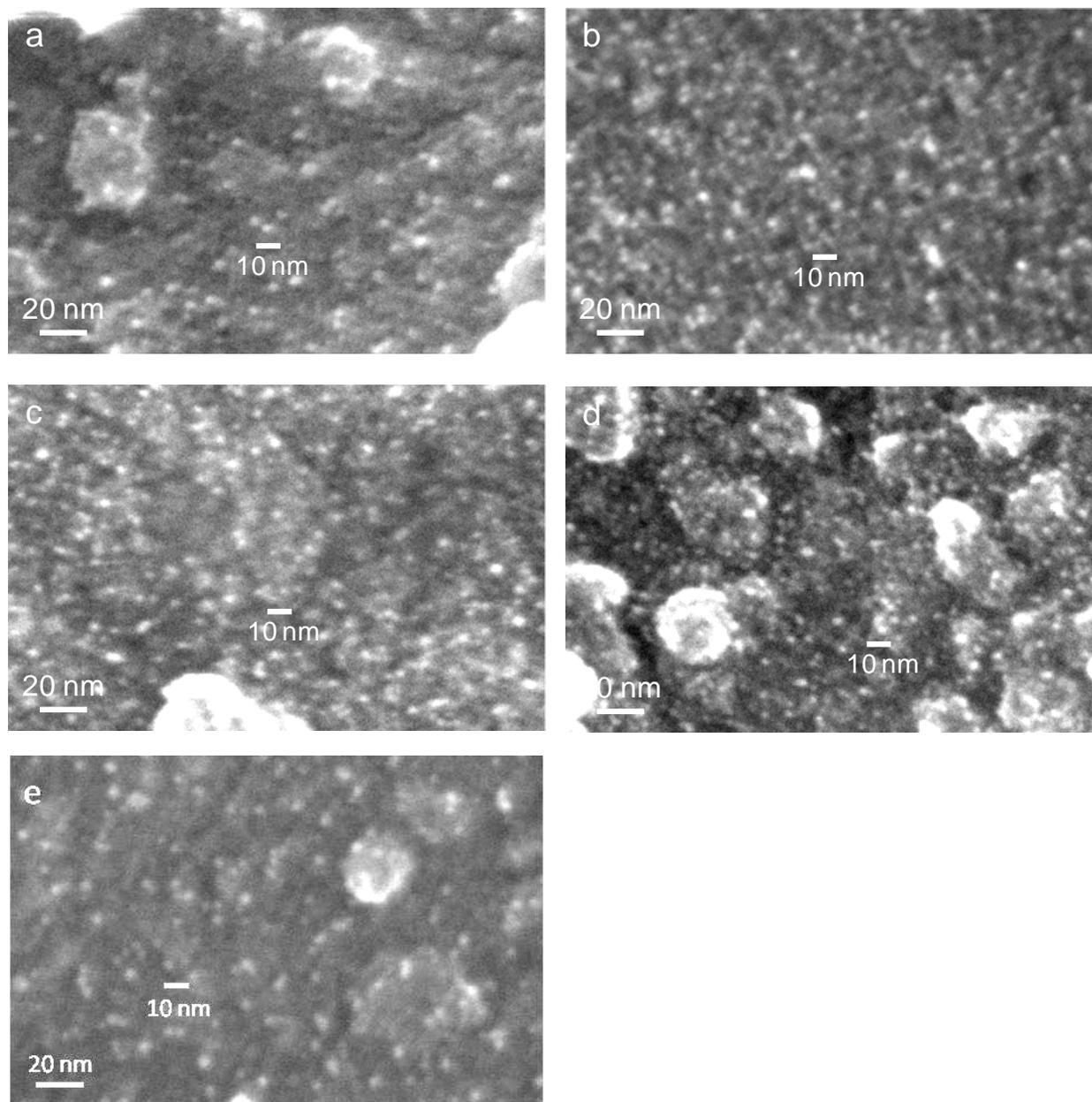
Jeremy J. Pietron<sup>\*</sup>, Michael B. Pomfret<sup>†</sup>, Christopher N. Chervin, Jeffrey W. Long, Debra R. Rolison<sup>\*</sup>

Surface Chemistry Branch, Code 6170, and <sup>†</sup>Chemical Dynamics and Diagnostic Branch, Code 6110  
U. S. Naval Research Laboratory, Washington, D.C. 20375, USA

### Supporting Information

*Deposition of Pt nanoparticles on RuO<sub>2</sub> nanoskins:* The surface morphology of as seen by scanning electron microscopy for Pt/RuO<sub>2</sub>(Ti) foil #4 (Pt/RuO<sub>2</sub>(Ti)-4) exhibits a sparse coverage of electrodeposited Pt nanoparticles (Fig. S1a), as described in the main text. Film Pt/RuO<sub>2</sub>(Ti)-6, shown in Fig. S1b, has a very similar apparent Pt particle size distribution to Pt/RuO<sub>2</sub>(Ti)-1 (Fig. 1). Foils 1 and 6 were fabricated in parallel at each stage—i.e., RuO<sub>2</sub> was electrolessly deposited on the two Ti foils in the same reactor at the same time; Pt nanoparticles were electrodeposited consecutively at the RuO<sub>2</sub>-coated Ti foils from the same H<sub>2</sub>PtCl<sub>6</sub> electrolytic solution. Foils 7 and 8 were similarly produced in parallel and feature Pt nanoparticle coverage (scanning electron micrographs shown in Figs. S1c and S1d) intermediate between the more dense coverage of films 1 and 6 and the more sparse coverage seen on Pt/RuO<sub>2</sub>(Ti)-2 (not shown) and Pt/RuO<sub>2</sub>(Ti)-4 (Fig. S1a). Foils 2 and 4, although similar in apparent Pt coverage, were fabricated in separate batches. The reason for the batch-to-batch variation is currently unclear; all of the films had very similar ( $\pm \sim 10\%$ ) electrochemical capacitance, making differences in RC time constants for charging of the electrode interface unlikely to be the source of the differences in Pt coverage. Experiments are underway featuring shorter deposition times and higher H<sub>2</sub>PtCl<sub>6</sub> concentration to determine if Pt nanoparticle size can be minimized without sacrificing effective Pt nanoparticle coverage of the RuO<sub>2</sub> films. The effect of surface morphology on electrodepositing Pt at a RuO<sub>2</sub> surface film comprising three sequentially deposited layers of RuO<sub>2</sub> nanoskin (Pt/RuO<sub>2</sub>(Ti)-5; Fig S1e) can be seen to be comparable to electrodeposition at the thinner, single layer RuO<sub>2</sub> nanoskins.

*Determination of electrochemical surface area of Pt on Pt/RuO<sub>2</sub> using underpotential deposition of copper:* The deposition and the stripping are performed in aqueous CuSO<sub>4</sub> solution, as described by Green and Kucernak.<sup>1</sup> One difference between the appearance of the voltammogram for Pt/RuO<sub>2</sub>(Ti) versus that for Pt black<sup>1</sup> is the absence of the obvious cathodic wave at Pt/RuO<sub>2</sub>(Ti) foil, which indicates that re-deposition of Cu<sub>UPD</sub> on the Pt/RuO<sub>2</sub>(Ti) foil does not occur on the timescale of the experiment. This difference arises for interrelated reasons: Kucernak and Green perform the experiment at 10 mV s<sup>-1</sup>, while we perform it at 100 mV s<sup>-1</sup> to ensure superimposition of sharp Cu stripping waves atop the large capacitive response at Pt/RuO<sub>2</sub>(Ti). The Cu UPD process is slow,<sup>1</sup> and the tenfold shorter timescale in our experiment does not allow measurable Cu UPD to occur. The large pseudocapitance added to the voltammetric response by the RuO<sub>2</sub> nanoskin and its associated RC time constant exacerbates the same problem—while stripping of Cu<sub>UPD</sub> is fast enough to respond to the slight lag between the actual interfacial potential and the programmed potential, the deposition process is too slow to be electrochemically measured.



**Fig. S1:** Scanning electron micrographs of Pt supported at  $\text{RuO}_2$  nanoskins supported on Ti foil. **a.** Pt/ $\text{RuO}_2(\text{Ti})$ -4; **b.** Pt/ $\text{RuO}_2(\text{Ti})$ -6; **c.** Pt/ $\text{RuO}_2(\text{Ti})$ -7; **d.** Pt/ $\text{RuO}_2(\text{Ti})$ -8; **e.** Pt/ $\text{RuO}_2(\text{Ti})$ -4 (three layers of nanometric  $\text{RuO}_2$  are electrolessly deposited sequentially at the Ti substrate before electrodeposition of Pt nanoparticles); see Table S1 for the electrochemical data derived for these specimens. Note: the ~20–40-nm objects seen in some of the images are adventitious fine dust particles adhered to the samples.

**Table S1.** Extended data set comprising all Pt/RuO<sub>2</sub>(Ti) electrodes tested in this study

Pt/RuO <sub>2</sub> (Ti) Foil #	E <sub>p,a</sub> (V vs RHE)	E <sub>p,a</sub> subtracted (V vs RHE)	j <sub>p,EC</sub> (mA cm <sup>-2</sup> )*	i <sub>p,m</sub> (A g <sub>Pt</sub> <sup>-1</sup> )**
1	0.68	0.65	—	—
2	0.62	0.63	0.15	83
3	0.68	0.68	0.28	125
4 <i>(one-sided film)</i>	0.63	0.60	—	—
5 <i>three-layer film</i>	0.64	0.62	0.19–0.28	—
6	0.67	0.62	—	—
7	0.67	0.61	—	—
8	0.66	0.59	—	—
9	0.65	0.61	—	—
10	0.68	0.67	—	—

\* Normalized to the electrochemical surface area of Pt in the film

\*\* Normalized to the Pt mass in the film

— Indicates that the quantity was not measured

---

1. C. L. Green, A. Kucernak, J. Phys. Chem. B 106 (2002) 1036–1047.