

### Experimental Details:

**Chemicals.** Platinum (II) acetylacetonate ( $\text{Pt}(\text{acac})_2$ , 97%), tetraoctylammonium bromide (TOAB, 98 %), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich. Copper (II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ , 97%) were purchased from Aladdin. Oleylamine (OLA) was purchased from J&K Chemical. 1-dodecanethiol (DDT) and  $\text{KHCO}_3$  were purchased from Sinopharm Chemical. All the Chemicals were used without further purification.

**Synthesis of  $\text{Cu}_x\text{Pt}_{100-x}$  nanocubes.** The synthesis was carried out using standard airless procedures.  $\text{Pt}(\text{acac})_2$ ,  $\text{Cu}(\text{acac})_2$ , and TOAB were mixed in 10.0-ml ODE. The mixture was heated to 110 °C at a rate of 25 °C/min with vigorous stirring under the protection of argon stream. OLA and DDT were separately dispersed in ODE to make solutions at the concentrations of 0.6 mol/L and 0.2 mol/L, respectively, which were then injected into the mixture in sequence. The color of the solution turned bright yellow once all the chemicals were completely dissolved in the solvent, deeper dark with increasing temperature at a rate of 12 °C/min, and finally black at around 207 °C. After maintaining the reaction at 230 °C for 20 min, 0.20-mL OLA and 6.0-mL toluene were injected into the reactor in order to quench the reaction.

These colloids were cooled to room temperature by quickly removing the heating source and put the reactor into cold water. Once cooled down, the solution was separated into two tubes containing 50.0-mL n-hexanol, followed by centrifugation (4,150 rpm for 8 min). After the first centrifugation, the n-hexanol was discarded, followed by another centrifugation. For the third centrifugation (4,150 rpm for 8 min), ethanol was added into the tubes to reach 30.0 mL of the total volume. The precipitate was re-dispersed in 1.0 mL of hexane in a bottle for further characterizations.

**Synthesis of pure Cu nanocubes.** The synthesis was carried out by following the established protocol.<sup>S1</sup> In a standard synthesis, 21-mg  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (the precursor),

50-mg glucose (the reductant), 90-mg 1-hexadecylamine (HDA, the capping agent), and 10-mL water (the solvent) were mixed in a glass vial and capped, and the final solution was magnetically stirred at room temperature overnight. The vial was then transferred into oil bath and heated at 100 °C for 6 h under magnetic stirring. The resultant products were isolated by centrifugation and washed with hot water (60 °C) for several cycles. The Cu nanocubes were finally re-dispersed in 3 ml of hot water (60 °C) for further characterizations.

**Synthesis of pure Pt nanocubes.** The synthesis was carried out by following the established protocol.<sup>S2</sup> In a standard synthesis, 0.05-mmol Pt(acac)<sub>2</sub>, 8.0-mL OLA and 2.0-mL oleic acid were loaded into a three-neck flask and heated to 130 °C under an argon stream. 0.14-mmol W(CO)<sub>6</sub> was then added into the solution. The temperature was subsequently raised to 240 °C and kept for 30 min with stirring. The resultant products were isolated by centrifugation and washed with anhydrous hexane for several cycles. The Pt nanocubes were finally re-dispersed in 3 ml of hexane for further characterizations.

**Sample characterizations.** A drop of the aqueous suspension of particles was placed on a piece of carbon-coated copper grid and dried under ambient conditions. TEM and HRTEM images were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV.

Powder X-ray powder diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-K $\alpha$  X-ray as the excitation source. The expected charging of samples was corrected by setting the C 1s binding energy of the adventitious carbon to 284.5 eV.

Cu<sub>x</sub>Pt<sub>100-x</sub> nanocubes were dissolved with a mixture of HCl and HNO<sub>3</sub> (3:1, volume ratio)

which was then diluted with 1% HNO<sub>3</sub>. The concentrations of Cu and Pt were then measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS).

**Catalyst preparation.** Cu<sub>x</sub>Pt<sub>100-x</sub> nanocubes were dispersed in hexane. Then the droplets of the suspension were repeatedly placed on the two sides of Ti foil electrode surface (1 cm × 2 cm for each side), followed by evaporation of the hexane at room temperature. Finally homogeneous spreading of 1.0-mg amount of Cu<sub>x</sub>Pt<sub>100-x</sub> nanocubes was made on the electrode surface. The Cu<sub>x</sub>Pt<sub>100-x</sub> nanocubes were annealed in Ar at 200 °C for 2 h to remove the surfactant. After cooling down to room temperature, a catalyst layer free of organic additives that has strong adhesion and mechanical stability was formed on the Ti foil.

**Electrochemical measurements.** The electrochemical measurements and CO<sub>2</sub> reduction experiments were carried out in a conventional three-electrode cell. CHI 660D electrochemical station (Shanghai Chenhua, China) was used to conduct CO<sub>2</sub> reduction experiments in aqueous 0.5-M KHCO<sub>3</sub> saturated with CO<sub>2</sub> at pH of 7.27. All potentials were measured with a 99.9% platinum foil as counter electrode against an Ag/AgCl reference electrode. The experiments were performed in a gas-tight three-compartment electrochemical cell separated by an anion exchange membrane (Nafion<sup>®</sup> 117). Two of the compartments contained 12-mL electrolyte and approximately 15-mL headspace, and the other contained 6-mL electrolyte. Prior to the experiments, the electrolyte in the cathodic compartment was saturated with CO<sub>2</sub> by bubbling CO<sub>2</sub> gas for at least 30 min. During the CO<sub>2</sub> reduction experiments, the electrolyte in the cathodic compartment was stirred at 300 rpm. All of the electrochemical measurements were conducted at room temperature, and recorded at a scan rate of 50 mV·s<sup>-1</sup> between -2.0 and -0.5 V (vs. Ag/AgCl). For CO<sub>2</sub> reduction, the electrochemical reaction ran for 0.5 h at -1.75 V. The CO<sub>2</sub> reduction products of Cu<sub>x</sub>Pt<sub>100-x</sub> nanocubes were analyzed using gas chromatography (GC). CO is converted to CH<sub>4</sub> by a nickel methanation reactor and then analyzed by a flame ionization detector (FID), while H<sub>2</sub> and CH<sub>4</sub> are

determined using a thermal conductivity detector (TCD) and a FID, respectively (see GC parameters in Table S1 and GC pneumatic circuit diagram in Figure S9).

The faradaic efficiency (FE) for CO, H<sub>2</sub> and CH<sub>4</sub> were calculated as below:

—

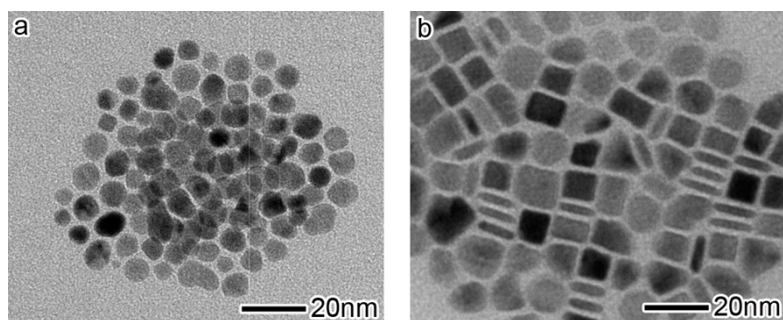
where:

$v_j$  (vol%) = volume concentration of  $j$  (CO, H<sub>2</sub> or CH<sub>4</sub>) in the gas from the electrochemical cell (according to GC data);

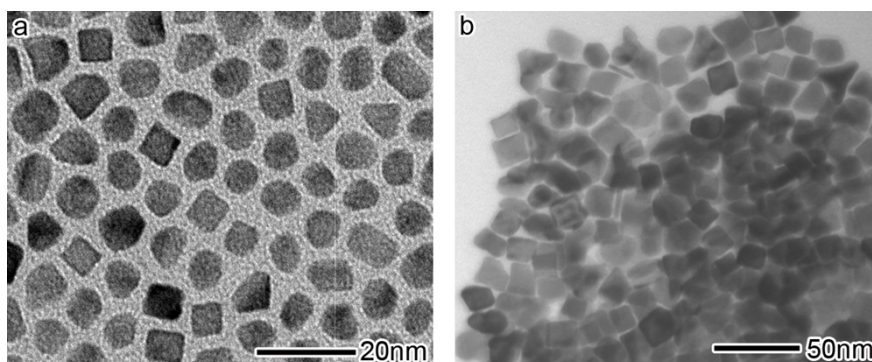
$V$  (mL at room temperature and ambient pressure) = 15 mL (gas volume at the top air chamber of the electrochemical cell);

$Q_{total}$  (mC) = total quantity of electricity;

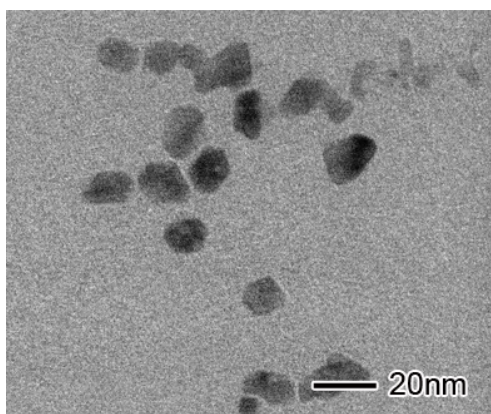
$p_0 = 1.01 \times 10^5$  Pa;  $T_0 = 273$  K;  $F = 96485$  C·mol<sup>-1</sup>;  $R = 8.314$  J·mol<sup>-1</sup>·K<sup>-1</sup>.



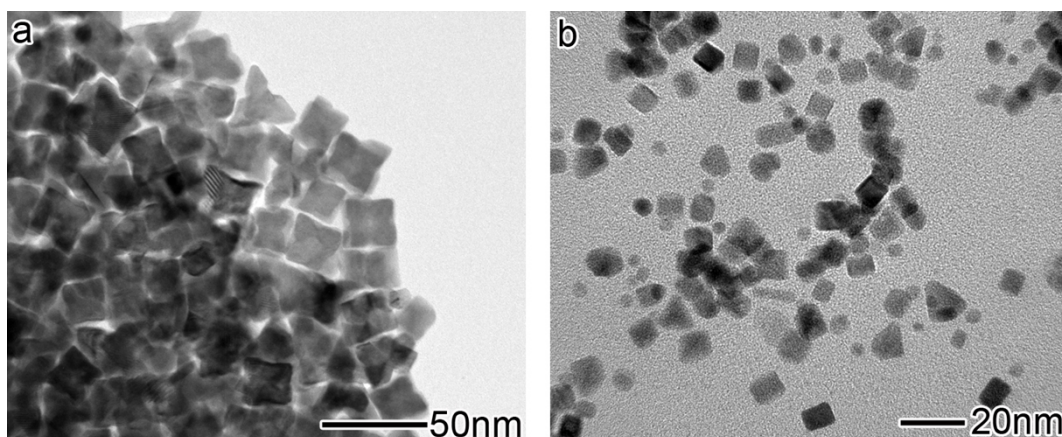
**Figure S1.** TEM images of the  $\text{Cu}_{68}\text{Pt}_{32}$  nanocubes synthesized under the same conditions as those for  $\text{Cu}_{68}\text{Pt}_{32}$  in Figure 1c, except for the use of different amounts of OLA: (a) 0.50 mmol OLA, and (b) 1.50 mmol OLA.



**Figure S2.** TEM images of the  $\text{Cu}_{68}\text{Pt}_{32}$  nanocubes synthesized under the same conditions as those for  $\text{Cu}_{68}\text{Pt}_{32}$  in Figure 1c, except for the use of different amounts of TOAB: (a) 0.30 mmol TOAB, and (b) 1.00 mmol TOAB.



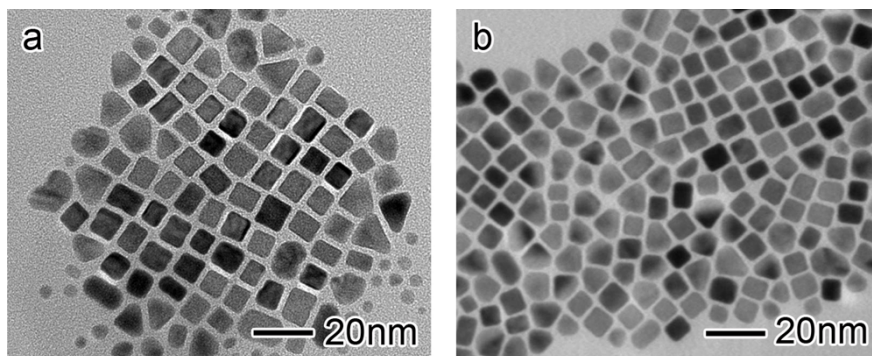
**Figure S3.** TEM images of the Cu<sub>68</sub>Pt<sub>32</sub> nanocubes synthesized under the same conditions as those for Cu<sub>68</sub>Pt<sub>32</sub> in Figure 1c, except for the use of 0.50 mmol of CTAB instead of TOAB.



**Figure S4.** TEM images of the  $\text{Cu}_x\text{Pt}_{100-x}$  nanocubes synthesized under the same conditions as those for  $\text{Cu}_{68}\text{Pt}_{32}$  in Figure 1c, except for the use of different amounts of DDT: (a) 0.12 mmol of DDT, and (b) absence of DDT.

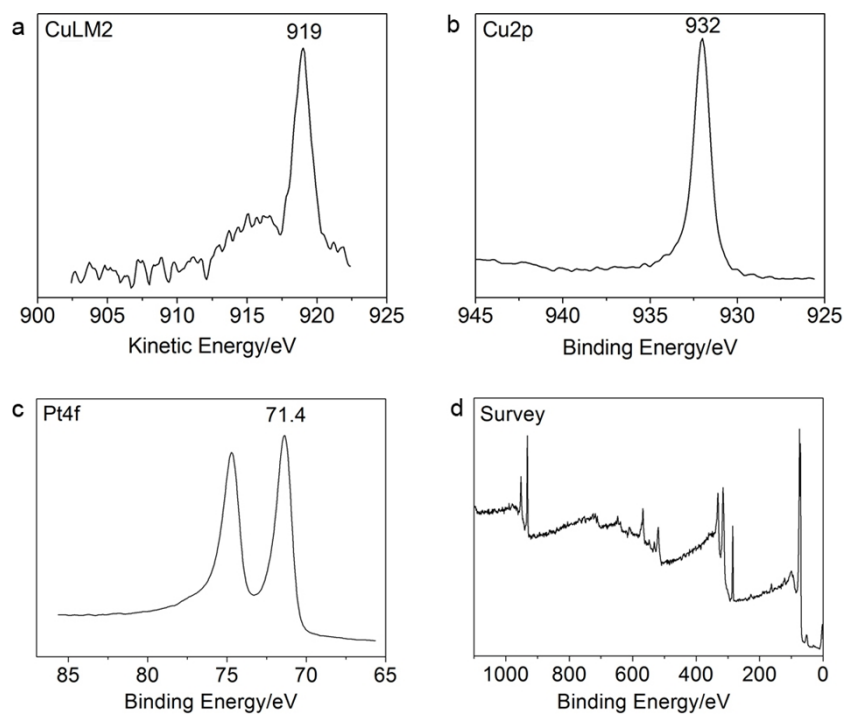
ICP-MS measurements show that the compositions of samples in Figure S4a and Figure S4b are  $\text{Cu}_{68}\text{Pt}_{32}$  and  $\text{Cu}_{65}\text{Pt}_{35}$ , respectively.



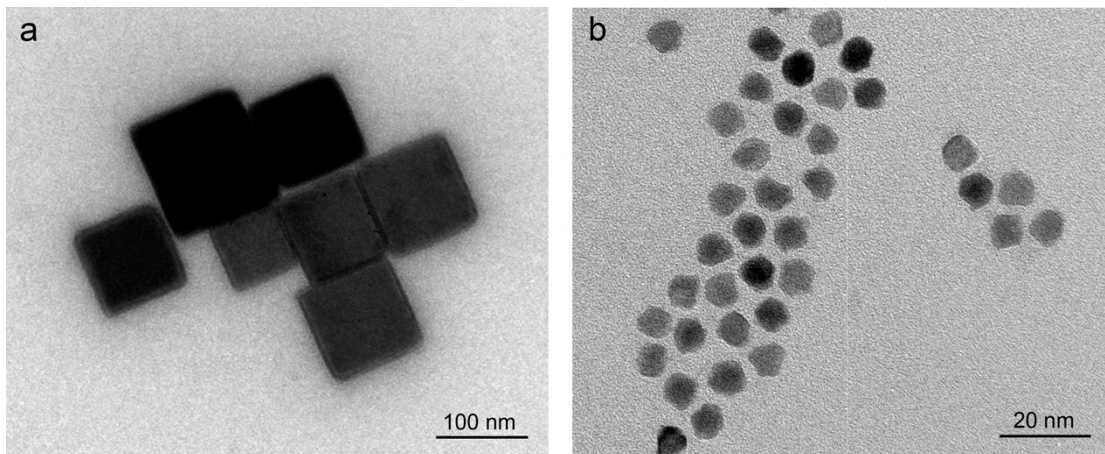


**Figure S5.** TEM images of  $\text{Cu}_{68}\text{Pt}_{32}$  alloy nanocubes (a) that were freshly synthesized, and (b) that have been dispersed in hexane for 3 months.

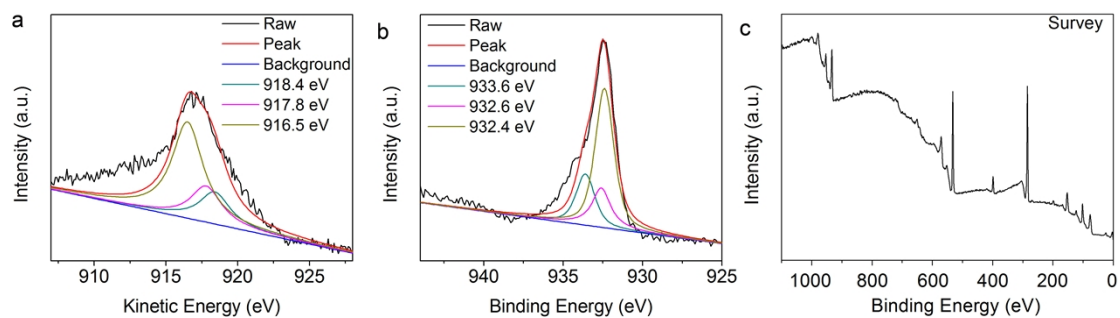
As indicated by the TEM images (Figure S5), no distinct morphological change has been observed after the 3-month storage.



**Figure S6.** XPS spectra of  $\text{Cu}_{68}\text{Pt}_{32}$  alloy nanocubes that have been dispersed in hexane for 3 months: (a) CuLM2, (b) Cu2p, (c) Pt4f and (d) survey spectra.

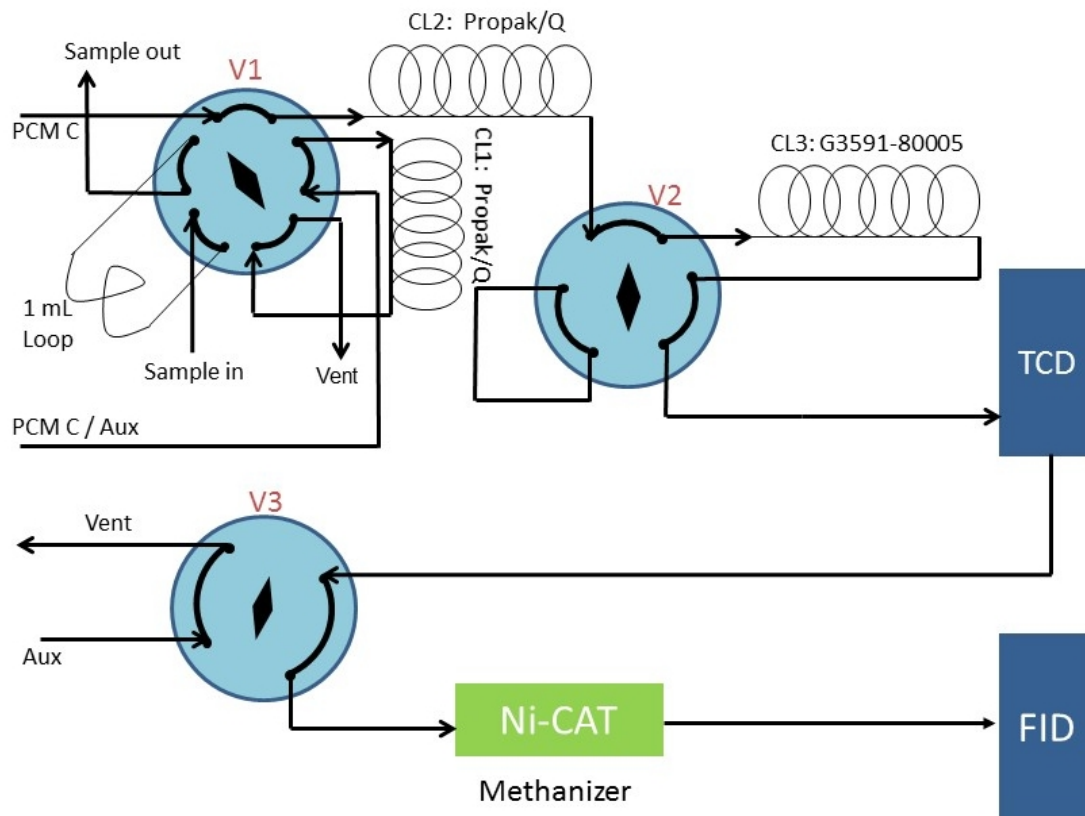


**Figure S7.** TEM images of reference samples: (a) pure Cu nanocubes, and (b) pure Pt nanocubes.



**Figure S8.** XPS spectra of Cu nanocubes that have been dispersed in water for 10 days: (a) CuLM2, (b) Cu2p and (c) survey spectra.

The XPS spectra in Figure S8 indicate that part of Cu(0) has been oxidized into Cu(I) and Cu(II) after dispersed in water for 10 days, according to the shifts of Cu LMM binding energy from  $\sim 919$  eV and Cu  $2p_{3/2}$  binding energy from  $\sim 932$  eV.<sup>S3</sup>



**Figure S9.** GC pneumatic circuit diagram.

**Table S1.** GC parameters.

|                  |  |
|------------------|--|
| Equipment        | Agilent 7890A GC   |
| Valve box heater | 80 °C  |
| Inlet            | Split ratio (3:1)  |
| Sample volume    | 1 mL   |
| Column           | Agilent Plot/Q   |
|                  | Agilent G3591-80005  |
| Carrier gas      | He, constant flow of 20 mL/min   |
| Oven             | 60 °C (13 min)   |
| Methanizer       | Ni Catalyst (375 °C)   |
| Detector         | FID, 300 °C, H <sub>2</sub> flow of 55 mL/min, Air flow of 500 mL/min,<br>make-up gas N <sub>2</sub> flow of 10 mL/min |
|                  | TCD, 250 °C, Reference flow of 15 mL/min,<br>make-up gas He flow of 5 mL/min   |
| Aux Heater       | 375 °C   |
| Valve events     | 0.05 min: Valve 1 on (start of sampling)   |
|                  | 2.6 min: Valve 2 on (switched for CO <sub>2</sub> to bypass MolSieve column)   |
|                  | 3.6 min: Valve 1 off (finish of sampling)  |
|                  | 4.8 min: Valve 3 on (start of CO <sub>2</sub> vent)  |
|                  | 6.2 min: Valve 2 off (finish of CO <sub>2</sub> vent)  |
|                  | 8.5 min: Valve 3 off (switched to send the separated remaining gases from MolSieve column to TCD)                      |

## References:

- S1. M. S. Jin, G. N. He, H. Zhang, J. Zeng, Z. X. Xie and Y. N. Xia, *Angew. Chem. Int. Ed.*, 2011, **50**, 10560-10564.
- S2. D. Xu, S. Bliznakov, Z. Liu, J. Fang and N. Dimitrov, *Angew. Chem. Int. Ed.*, 2010, **49**, 1282-1285.
- S3. W. Kautek and J. G. Gordon II, *J. Electrochem. Soc.*, 1990, **137**, 2672-2677.