Influence of Copper on Trivalent Chromium Conversion Coating Formation on Aluminum

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In the present work, modified copper-containing trivalent chromium conversion (TCC) coating processes for aluminum were investigated. The copper addition to the TCC bath was made for the purposes of reducing the generation of hydrogen peroxide and chromium (VI) species during the coating growth. The morphologies and compositions of the coatings were examined using high-resolution electron microscopy, energy-dispersive X-ray spectroscopy and Raman spectroscopy. UV photometric measurements were employed to determine the amount of hydrogen peroxide in the TCC solution. The resulting coatings contained zirconium oxides, chromium hydroxide and fluorides and sulfate constituents, as well as copper oxides and copper-rich deposits that were preferred cathodic sites for oxygen reduction. Of most significance, no chromium (VI) species were detected in the coatings by Raman spectra. It is suggested that this results from reduced generation of hydrogen peroxide, as disclosed by photometric measurements, at the cathodic copper-rich particles, due to favoring of the four electron oxygen reduction reaction.

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Trivalent chromium conversion (TCC) coatings are promising eco-friendly alternatives to chromate conversion coatings due to the lower toxicity of trivalent chromium species compared with hexavalent chromium.1 The TCC coating solution can be regarded as a modified Zr-based conversion coating solution with addition of small amounts of trivalent chromium salts.2,3 Our previous work used scanning electron microscopy and atomic force microscopy to reveal cracking and spalling of the coating formed on superpure aluminum, especially after a prolonged conversion treatment.4 This was associated with the fast kinetics of aluminum dissolution due to the attack by fluorine ions in the reaction solution and the stress in the coating.5 In contrast, the TCC coating formed on AA2024 alloy suppressed the oxygen reduction reaction, due to the physical barrier created by the Zr-/Cr-rich coatings,1,6,7 and the coating displayed improved adhesion, although the coating was significantly thinner than that formed on superpure aluminum.

With respect to the effect of copper alloying, George et al.8 investigated binary alloys containing 1, 5, and 25 at.% Cu prepared by magnetron sputtering and revealed a decrease in the coating growth rate of zirconium-based coatings with increase of the Cu/Al ratio. This was suggested to be due to the copper species present in the coating impeding the cation transport to the coating base. Furthermore, a layer of corrosion products formed at the coating base. Cerezo et al.9–11 modified the Zr-based conversion coating solution by adding a small amount of copper salts (30–50 ppm). The copper components, which had a high deposition tendency, formed copper and/or copper oxide agglomerates on the substrate, which created local alkalinity that supported the coating formation. As a consequence, the coating thickness on the multi-metal substrate (AA1060, cold rolled steel and hot dip galvanized steel) was increased.

One concern about TCC coatings has been the possibility of oxidation of Cr(III) species to form Cr(VI) species either during or following coating growth on aluminum. Cr(VI) species were reported to be present in the freshly-formed TCC coatings, but were undetectable in the case of a fresh coating on AA2024 alloy.12,13 A generally accepted hypothesis for the formation of Cr(VI) species is that hydrogen peroxide created by the oxygen reduction reaction can oxidize Cr(III) species in the coating.12,13 Furthermore, the presence of hydrogen peroxide during the conversion treatment of aluminum specimens was supported by the results of a recent study that used UV spectrophotometry.14

In the present work, modified TCC coating solutions were prepared by addition of either 0.05 g/L or 0.5 g/L CuSO4 to a SurTec 650 solution (a commercial TCC coating solution). The influence of the additions on the kinetics of coating growth was investigated using high-resolution scanning electron microscopy and transmission electron microscopy. Raman spectroscopy and UV spectrophotometry were used to study the coating chemistry, particularly the chromium valence state in the coating and the presence of hydrogen peroxide in the reaction solution, respectively.

Experimental

Conversion treatments.—Specimens of high-purity aluminum, of dimensions of 30 × 20 × 0.3 mm, were electropolished in a mixture solution of 60 wt% perchloric acid and 80 v/v% ethanol (1:4 v/v, <10°C) at 20 V for 4 min. After electropolishing, the specimens were rinsed in ethanol and deionized (DI) water, followed by drying in a cool air stream.

SurTec 650 chromitAL (SurTec Corp.), a commercial trivalent chromium solution (Zr:Cr atomic ratio = ∼0.7), was diluted with DI water in a ratio of 1:4 by volume. Subsequently, either 0.05 g/L or 0.5 g/L copper sulfate (CuSO4, Sigma-Aldrich, U.K.) was dissolved in the solution. The pH of the solutions was then adjusted to 3.9 by adding droplets of 1 wt% NaOH and/or 5 wt% H2SO4. In order to form the coatings the aluminum, specimens were immersed in the solutions for different times, followed by immersion in DI water at 40°C for 120 s, rinsing in DI water for 5 s, and drying in a stream of cool-air.4

In contrast, some aluminum specimens were immersed in 0.01 M sodium fluoride solution containing either 0.05 g/L or 5 g/L copper sulfate. The specimens were prepared to assist understanding of the coating growth in the copper-containing TCC bath. The pH value of the copper-containing NaF solutions was adjusted to 3.9 by adding 5 wt% H2SO4 and 1 wt% NaOH.

Open-circuit potential (OCP) measurements during coating formation were made for selected specimens using a Solarton electrochemical workstation with a ModuLab software controller.

The exposed area of each specimen was ∼2.25 cm². A saturated calomel electrode (SCE, E° = 0.241 V vs. NHE) was employed as the reference electrode.

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Coating characterization.—The surfaces of coatings were revealed by the secondary electron images recorded by scanning electron microscopy (SEM), using a Zeiss Ultra 55 instrument with an energy-dispersive X-ray spectroscopy (EDS) facility. Accelerating voltages of 3 kV and 15 kV were used for SEM and EDS, respectively. The SEM/EDS data for each specimen were recorded at three different points and processed by the INCA software (version 4.09). A JEOL 2000 FX II instrument, operated at an accelerating voltage of 120 kV, was used to examine electron transparent thin cross sections of specimens that were prepared by ultramicrotomy as described previously. In order to examine the coating chemistry, a Renishaw 2000 Raman instrument with a 514 nm argon laser excitation was used. The instrument was controlled using GRAMS/32 and WIRE Video View software. The integration time was 30 s, with 10 times accumulation to avoid the effect of stray light noise. The area of the laser beam on the specimen surface was about 1 μm in diameter. Prior to the specimen examination, the argon laser was calibrated at 520 cm⁻¹ using a standard silicon panel. Raman spectra were collected at the frequency range of interest between 1200 and 2000 cm⁻¹. Triplicated measurements were made that showed good reproducibility.

Hydrogen peroxide measurement.—In order to investigate hydrogen peroxide generation, a photometric method using a titanyl reagent (3 M H₂SO₄, 0.05 M Cr₂O₇₂⁻ and DI water of 1:1:4 by volume) was employed. Aluminum specimens, of dimensions 30 × 20 × 0.3 mm, were first ground to a 1200 SiC grit finish, followed by 1 wt% HCl etching at room temperature for 5 s to activate the surface and rinsing in DI water for 15 min. Specimens were then immersed in 250 ml of each of the four solutions listed in Table I at a temperature of 40°C. The solutions comprised (i) 0.01 M sodium fluoride, (ii) 0.01 M sodium fluoride + 0.05 g/L copper sulfate, (iii) 0.01 M sodium fluoride + 0.05 g/L copper sulfate + 0.01 M chromium nitrate + 0.015 M potassium fluorozirconate. The pH of each solution was adjusted to 3.9 by adding droplets of 5 wt% H₂SO₄. The solutions, which were contained in a glass beaker, were stirred to enhance mass transport to the substrate/solution interface. A cuvette was used to contain a mixture of 1 ml of the test solution and 2 ml of the titanyl reagent. The solution was collected after immersion of the aluminum for 0, 300, 600, 1200, 1800, 3600 and 5400 s. A UV-vis spectrophotometer (UV-3000, MAPADA) was employed to investigate the absorbance at 400 nm of the mixture solutions in the cuvette. The concentration of hydrogen peroxide in the test solutions was determined from the absorbance (Aₜ₂₅₀) using the relation reported previously: H₂O₂ concentration (μM) = 2950 × Aₜ₂₅₀. Furthermore, a careful check was made using a 100 mM H₂O₂ solution alone and mixed solutions containing 100 mM H₂O₂ and either 0.05 or 0.5 g/L CuSO₄. The photometric results showed that the presence of copper ions did not interfere with detection of hydrogen peroxide using the titanyl reagent. All measurements were repeated three times for a particular condition in order to ensure good reproducibility of the data with errors of less than 3%. All chemical reagents in the present work were of analytical grade, DI water of resistivity 18 MΩ cm⁻² was used to prepare solutions and to clean specimens.

### Table I. Codes used to designate solutions used for determining the influence of copper species on H₂O₂ formation during conversion treatment of aluminum.

| Solution codes | Compositions |
|----------------|--------------|
| F + Acid       | 0.01 M NaF, pH 3.9 |
| Cu + F + Acid  | 0.05 g/L CuSO₄ and 0.01 M NaF, pH 3.9 |
| Cu + Cr(III) + F + Acid | 0.05 g/L CuSO₄ + 0.01 M Cr(NO₃)₃ and 0.015 M K₂ZrF₆ and 0.01 M NaF, pH 3.9 |

### Results and Discussion

Copper components in the reaction solution.—Figure 1a displays the OCP of the aluminum during immersion for 5400 s in 0.01 M sodium fluoride solution containing either 0.05 or 0.5 g/L CuSO₄ solutions for (a) 5400 and (b) 300 s.

![Figure 1a](image1.png)  
**Figure 1a.** Open-circuit potential of aluminum during treatment in 0.01 M sodium fluoride solution with additions of either 0.05 or 0.5 g/L CuSO₄ solutions for (a) 5400 and (b) 300 s.

![Figure 1b](image2.png)  
**Figure 1b.** Open-circuit potential of aluminum during treatment in 0.01 M sodium fluoride solution with additions of either 0.05 or 0.5 g/L CuSO₄ solutions for (a) 5400 and (b) 300 s.

Copper component analyses (not shown here) revealed that the bright particles were copper-rich deposits that were formed at surface defects or residual flaws in the alloy.
The particle coverage was analyzed by the ImageJ software, employing a threshold to distinguish the matrix and particle regions. Using SEM images at the same magnification, areal coverages of 5.5 and 13.1% were obtained for the surfaces immersed in the solutions containing 0.05 g/L and 0.5 g/L copper sulfate, respectively. The greater coverage at the higher copper concentration led to the observed increase in the OCP.

Coating formation.---Figure 3 displays the OCPs of aluminum specimens during conversion treatment for 1800 s in the SurTec solutions containing 0.05 and 0.5 g/L copper sulfate and compares these with the OCP obtained in earlier work using a copper-free SurTec bath. The OCPs in the three solutions initially fall to a minimum and then increase to approximately constant final values, of about $-1.5, -0.85$ and $-0.3 \text{ vs SCE}$ for the reference, 0.05 and 0.5 g/L CuSO$_4$-containing solutions, respectively. The respective minima were about $-1.55, -1.1$ and $-1.1 \text{ vs SCE}$. The minimum in potential occurs at an earlier time for the copper-containing solutions. This is possibly due to the deposition of copper and the subsequent increase of cathodic activity on the aluminum surface. The enhanced local alkalinity generated by oxygen reduction may increase the oxidation of the aluminum, by more extensive thinning of the passive film, leading to a more rapid decrease in the potential. The positive potential shifts in the copper-containing solutions are associated with deposited copper, which is revealed in the SEM micrographs of the specimen surfaces shown in Figures 4 and 5. After immersion for 15 s in the 0.05 and 0.5 g/L CuSO$_4$-containing solutions (Figs. 4a and 4b, respectively) particles of diameters less than 1 μm, evident as bright features in the backscattered electron images, that were copper-rich according to EDS analysis, covered ∼4.8 and 8.1% of the respective surfaces. Point EDS analyses at locations of particles revealed much greater amounts of zirconium and chromium relative to the amounts elsewhere on the coated surface (Table II). After conversion treatment for 300 s the sizes of the copper-rich particles increased and agglomerates of up to 10 μm
sections of the coatings at locations on the aluminum surface remote from copper-rich particles, although variability in the thickness of the coating across the aluminum substrate cannot be ruled out.

**Coating and solution chemistry.**—Raman spectroscopy, which had an analysis depth of several micrometers, was employed to examine the species present in the coatings by means of the vibrational shifts.\(^1\)\(^{13,21,22}\) Figure 7 shows Raman spectra after conversion treatment of the aluminum for 300 s in the modified SurTec 650 solutions with 0.05 (Figs. 7a and 7b) and 0.5 g/L (Figs. 7c and 7d) CuSO\(_4\) additions.

The spectrum of Figure 7a recorded at a region of coating on the aluminum substrate in the solution containing 0.05 g/L CuSO\(_4\) reveals peaks for CuO at ∼280 and ∼620 cm\(^{-1}\) and for CuF\(_2\) at 213 and 690 cm\(^{-1}\).\(^{12}\) Copper metal is deposited initially at cathodic sites on the aluminum surface. Deposited copper may subsequently be oxidized if it becomes electrically isolated from the aluminum substrate. The isolation may be achieved by the formation of coating material, which EDS analysis indicated developed preferentially at the deposits. The presence of fluoride ions in the formed coatings promoted the oxidation reaction of isolated copper particles.\(^{25–27}\) Stronger peaks due to CuO were revealed at the region of a particle (Fig. 7b) as evidenced by the peaks present at 280 cm\(^{-1}\). Notably, a satellite peak at 328 cm\(^{-1}\) associated with CuO excitation was detected on the coated surface of Figure 7a recorded at a region of coating on the aluminum substrate. The presence of the copper-rich deposits (Figs. 4 and 5) can result in surface-enhanced Raman scattering (SERS),\(^{28,29}\) which may explain the prominent Raman peaks that were associated with copper species, especially on the copper-rich particles.

The Raman shifts at 450 and 540 cm\(^{-1}\) were associated with copper species, especially in the copper-rich particles (Figs. 4 and 5) can result in surface-enhanced Raman scattering (SERS),\(^{28,29}\) which may explain the prominent Raman peaks that were associated with copper species, especially on the copper-rich particles. The Raman shifts at 450 and 540 cm\(^{-1}\) were associated with copper species, especially on the copper-rich particles.

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**Table II.** SEM/EDS point analyses (wt%) of specimen shown in Figures 4a and 4b.

| Solutions      | Cu  | Cr  | Zr  |
|----------------|-----|-----|-----|
| Copper-free    |     |     |     |
| 0.05 g/L       |     |     |     |
| Matrix         | -   | 2.6 ± 0.2 | 0.3 ± 0.1 |
| Particles      | 9.3 ± 0.3 | 21.8 ± 1.1 | 10.7 ± 0.5 |
| 0.5 g/L        |     |     |     |
| Matrix         | 0.2 ± 0.1 | 2.1 ± 0.1 | 0.7 ± 0.1 |
| Particles      | 82.3 ± 1.2 | 3.6 ± 0.4 | 1.6 ± 0.3 |

and (d-f) 300 s, in the copper-free SurTec solution\(^1\) (a, d) and solutions containing 0.05 g/L (b, e) and 0.5 g/L (c, f) copper sulfate. The cross-sections reveal a chromium- and zirconium-rich outer layer above a thin aluminum-rich layer that contains oxygen and fluorine species.\(^3\) The cracks through the coatings (Figs. 6c and 6d) may form due to dehydration of the coating that occurs in the laboratory air or under vacuum in the microscope.\(^3\) The coating thicknesses were analyzed using the ImageJ software. The results are presented in Table IV. After a treatment of 120 s, the coatings were of similar thickness, about 44 nm. After a treatment of 300 s, the coating thickness had increased to the range 68 to 78 nm. The coating formed in the solution containing 0.5 g/L CuSO\(_4\) revealed the lowest thickness. This is reversibly associated with the locally enhanced coating deposition at the copper-rich particles, although variability in the thickness of the coating across the aluminum substrate cannot be ruled out.

**Table III.** SEM/EDS point analyses (wt%) of specimen shown in Figures 5a and 5b.

| Solutions      | Cu  | Cr  | Zr  |
|----------------|-----|-----|-----|
| Copper-free    |     |     |     |
| 0.05 g/L       |     |     |     |
| Matrix         | -   | 2.6 ± 0.2 | 0.3 ± 0.1 |
| Particles      | 9.3 ± 0.3 | 21.8 ± 1.1 | 10.7 ± 0.5 |
| 0.5 g/L        |     |     |     |
| Matrix         | 0.2 ± 0.1 | 2.1 ± 0.1 | 0.7 ± 0.1 |
| Particles      | 82.3 ± 1.2 | 3.6 ± 0.4 | 1.6 ± 0.3 |

| Wt.% | O    | F    | Al   | S    | Cr    | Cu    | Zr    |
|------|------|------|------|------|-------|-------|-------|
| 0.05 g/L | Matrix | 2.1 ± 0.1 | 1.6 ± 0.3 | 96.7 ± 1.5 | N/D | 0.2 ± 0.1 | N/D | 0.4 ± 0.1 |
|       | Particles | 14.4 ± 1.0 | 1.8 ± 0.2 | 72.5 ± 1.0 | 0.3 ± 0.1 | 4.0 ± 0.2 | 1.4 ± 0.1 | 5.6 ± 0.8 |
| 0.5 g/L | Matrix | 2.1 ± 0.1 | 1.6 ± 0.3 | 96.7 ± 1.5 | N/D | 0.1 ± 0.1 | N/D | 0.5 ± 0.1 |
|       | Particles | 15.8 ± 0.4 | 3.1 ± 0.3 | 34.1 ± 0.9 | 0.3 ± 0.1 | 3.0 ± 0.1 | 35.4 ± 0.8 | 8.3 ± 0.6 |
Figure 6. Transmission electron micrographs of the coated matrix after conversion treatment of aluminum for (a-c) 120 and (d-f) 300 s, in the Sur Tec 650 solution with additions of (a, d) 0, (b, e) 0.05 and (c, f) 0.5 g/L CuSO4.

Table IV. Average coating thickness (nm) determined from TEM images in Figures 6.

| Thickness / nm | As-received | 0.05 g/L | 0.5 g/L |
|---------------|-------------|----------|---------|
| 120 s         | 42 ± 2.5    | 45 ± 2.1 | 44 ± 2.8 |
| 300 s         | 78 ± 3.4    | 70 ± 2.7 | 68 ± 3.8 |

particles (Fig. 7d) disclosed the presence of CuO (262 and 660 cm⁻¹), Cu₂O (700 cm⁻¹), chromium oxides/fluorides (545 cm⁻¹) and zirconium oxide (448 cm⁻¹). The difference of the Raman peaks associated with the coating components in Figs. 7b and 7d, for example, CuO at 280 and 262 cm⁻¹, respectively, may result from the effect of particle size on scattering. In addition, the Raman peak at 545 cm⁻¹ represents the presence of a mixture of chromium components, such as chromium oxide (550 cm⁻¹), chromium hydroxide (526 cm⁻¹) and chromium fluoride (538 cm⁻¹). With respect to zirconium oxide, the Raman peaks at 448 and 450 cm⁻¹ display negative shifts relative to the reported position at 476 cm⁻¹. This may result from the effect of contributions of aluminum oxide/hydroxide (438 cm⁻¹) and zirconium fluorides (450 cm⁻¹).

Notably, a Raman peak at 780–904 cm⁻¹, characteristic of Cr(VI), was not resolved in any Raman spectra in Figure 7. The region of the Cr(VI) peak is highlighted in Figure 8 for a Raman spectrum recorded from the TCC coated aluminum matrix after conversion treatment for 1200 s in SurTec 650 solution with addition of 0.05 g/L CuSO4.

Figure 7. (a, b) and (c, d) Raman spectra of TCC coatings formed on aluminum for 300 s in SurTec 650 solution with additions of 0.05 and 0.5 g/L CuSO4, respectively. (a, c) At the matrix and (b, d) at Cu-rich particles.

Figure 8. Raman spectrum of a TCC coating formed on aluminum for 1200 s in SurTec 650 solution with addition of 0.05 g/L CuSO4.
the longer time of 1200 s in the 0.05 g/L CuSO4-containing solution. The absence of a detectable amount of Cr(VI) species in the present coatings is proposed to be related to reduced generation of hydrogen peroxide during conversion treatment of aluminum in the modified solutions, which is supported by the following measurements.

The results of photometric measurements of hydrogen peroxide formed in the solutions listed in Table 1 are presented in Figure 9. The curves show that the rate of generation of hydrogen peroxide is highest at the start of the period of immersion and subsequently slows to a relatively constant value. In the 0.1 M NaF solution (pH = 3.9, adjusted by 5 wt% H2SO4 droplets), the concentration of hydrogen peroxide rapidly increased up to ~90 μM at 300 s and then rose more slowly to ~170 μM at 5400 s. The greatest amount of hydrogen peroxide was detected in the acidified solution containing 0.01 M sodium fluoride. The amount was significantly reduced by the addition of 0.05 g/L copper sulfate, for example, to ~47 and 100 μM after immersion for 1200 and 5400 s, respectively, compared with ~145 and 180 μM H2O2 respectively. However, with further modifications of the solution composition by additions of either 0.01 M Cr(NO3)3, 0.01 M Cr(NO3)3, + 0.015 M K2ZrF6, the concentration of hydrogen peroxide was decreased to still lower levels of 18 and 10 μM, respectively after immersion for 5400 s. Notably, the copper-free SurTec 650 solution contained zirconium and chromium salts, sodium fluoride and sulfates and the atomic ratio of zirconium relative to chromium is 0.7. Therefore the solution containing 0.01 M Cr(NO3)3, 0.015 M K2ZrF6, 0.1 M NaF and 0.1 M NaNO3 simulates the commercial SurTec solution used in this work. In comparison with our previous work, a significant reduction of hydrogen peroxide generation was revealed during aluminum immersion in the copper-free solutions containing 0.01 M Cr(NO3)3, or 0.01 M Cr(NO3)3, + 0.015 M K2ZrF6. The results indicate that the addition of copper sulfate to the reaction solutions can inhibit the hydrogen peroxide generation during conversion treatment of aluminum even after prolonged immersion. One reason is associated with the enhanced cathodic reaction around the copper-rich particles in the oxygen reduction reaction. Jakab et al. used the L x LT copper surface to simulate the copper coverage on AA2024 alloy, and the results revealed that the four-electron charge-transfer oxygen reduction reaction rate increased linearly with copper coverage. Furthermore, Colley et al. applied copper microelectrodes (25 μm diameter) to disclose the number electrons involved in the reduction reaction increased toward 4 as the mass transport rate decreased. Thus, it is proposed that the reduction in hydrogen peroxide generation observed with the addition of copper sulfate to the conversion coating solutions is associated with promotion of a four electron oxygen reduction reaction (ORR) rather than a two-electron reaction. Notably, our previous paper revealed a copper-enriched layer, a few nanometers thick, at the base of conversion coatings. Its formation is associated with the nobility of copper relative to aluminum. The enrichment develops during pre-treatments of the substrate and is maintained during coating growth. No evidence has been found of an influence of the enrichment on Cr(VI) formation. In contrast, the dissolved oxygen in the coating bath was involved in the generation of Cr(VI), which we attributed to the production of hydrogen peroxide in the two-electron reduction of oxygen. In addition, the reduction mechanism will be investigated by the authors in future studies using a rotating disk electrode. In addition, the effect of copper additions to the reaction solution on chromate formation during corrosion and air exposure of the coated aluminum also requires examination.

Conclusions

1. Copper-rich deposits were formed on aluminum after conversion treatment in either 0.1 M sodium fluoride solutions or Sur Tec 650 conversion coating solutions, containing additions of copper sulfate. The copper-rich deposits led to increased an open-circuit potential due to an increased rate of the oxygen reduction reaction.

2. The coatings formed in the copper-containing solution (0.5 g/L) revealed numerous surface cracks and regions of spallation, while such coating defects were relatively negligible in the coatings formed in the modified solution containing 0.05 g/L CuSO4.

3. Raman spectra of the coated matrix and particles revealed the presence of copper oxides, zirconium oxides, chromium hydroxide and fluorides and sulfate constituents, while hexavalent chromium species were undetectable.

4. UV photometric measurements were successfully applied to demonstrate the generation of hydrogen peroxide during the conversion treatment of aluminum in the trivalent chromium solutions.

5. The addition of copper sulfate to a TCC solution can reduce the amount of hydrogen peroxide generated by the oxygen reduction reaction by promoting a four-electron reaction at the copper-rich regions.

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