Enhanced durability of gold-coated current collectors for high power electrochemical devices†

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A highly durable current collector by optimizing the Au electrochemical deposition conditions is reported. The high corrosion resistance of the Au layers on the current collector is successfully modified by adjusting the applied current densities and utilizing pulse potentials. The optimized Au-coated current collector is evaluated as the electrode substrate portion of the electrochemical cell.

Because of the dramatic progress in electronic and electrochemical devices with diverse platforms, technology advancements for the current collector are required to ensure the improved performance of the devices.1–3 With the development of the devices, the stability of the current collector, such as the printed circuit board (PCB), which is an essential component in the devices, often suffers from a harsh operating environment.4 Most of the high performance devices operate under high power and enormously exothermic conditions, causing high current-induced corrosion and heat damage on the surface of the current collector.5–6 Various types of electrolytes with different pH values and high operating voltages (e.g., ~1 V for fuel cells and ~4 V for Li batteries) can easily degrade and corrode the current collectors for electrochemical reactions, thereby gradually deteriorating the durability and performance of the energy devices.7–9 For example, direct methanol fuel cells, which have been considered as an alternative electrochemical energy conversion system for portable devices, encounter low stability issues of the cell during long-term operation due to corrosion of the current collector in the acidic environments.10 In this regard, the conventional PCB current collector has been designed with a gold (Au) coating layer on the conducting copper (Cu) or nickel (Ni) interlayers to resist corrosive conditions.11,12 In addition, the Au coating layer can effectively provide high electrical conductivity, and the interfacial Au alloy with an adjacent metal interlayer exhibits good contact resistance.11–15 The Au coating layer has been simply applied by the sputtering, electroless-deposition and electro-deposition methods.14 Among them, the electrochemical deposition method has been widely used as a versatile surface-finishing process in a variety of decorative, engineering and electroforming applications due to the facile control of the appearance and the properties of the deposited layer over broad ranges.16–19 Controlling electrochemical variables and engineering functional factors for Au coating via electrodeposition can effectively improve the quality of the coating layers, consequently providing durability and good performance of the electrochemical devices.20

In this study, we achieve the enhanced durability of the Au coating layer by tuning the electrodeposition variables for the highly resistive current collector of electrochemical devices. We diagnose the resistance of the electrodeposited Au coating layer by investigating the morphological features and electrochemical properties and by comparing the coating layers with an electroless-deposited Au layer as a reference. The Au coating layer is optimized by regulating the degree of applied current density for electrodeposition and introducing pulse electrodeposition. Finally, the electrochemical performance of the current collector employing the optimized Au coating layer is investigated to evaluate its quality and durability for electrochemical devices.

Fig. 1 shows the PCB current collector loaded with a polyimide polymer substrate, an intermediate metal layer (Cu and Ni), and an Au protection layer. The Au layer was applied by electroless deposition, typically showing a smooth surface feature, as revealed in Fig. 1a. The current collector was designed using the patterned polyimide substrate as the porous structure, enabling the construction of diverse shapes and allowing electrolyte penetration. Current collectors prepared using electroless deposition as the chemical deposition method often suffer from defects, such as pinholes (Fig. 1b), and are highly dependent on the pre-surface condition of the substrate.

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In addition, the highly sensitive electrolyte bath is easily degraded, which affects its long-term stability, and the mechanical properties of the Au layer are insufficient due to the low nucleation rate and nuclei size for electroless deposition. In this regard, the insufficient covering is located, and the Au-coated surface is easily removed by peeling (Fig. 1c and d). The uncovered coating area has defects, and the weak mechanical strength of the electroless-deposited Au layer negatively affects the stability of the current collector. Fig. 1e shows the image of the PCB current collector after the cell test, which was conducted in an acidic solution composed of 3 M methanol and 1 M H$_2$SO$_4$. Severe corrosion was observed, even with the naked eye, on the surface of the current collector. From the magnified SEM images of current collectors, pitting and large cracks were found on the electroless-deposited Au layer, indicating that many defects on the Au layer can cause initiation sites for corrosion in the acidic solution environment.

To solve this problem and to enhance the quality of the Au layer, we performed electrodeposition to introduce the Au coating layer and to control the deposition variables, such as the applied current densities. The electrodeposition method for the coating layer can offer improved coverage because of the substantial attraction of metal ions with a large electrochemical potential onto the surface. Moreover, the smaller nuclei size corresponding to a smaller grain size can improve the mechanical strength of the coating layer and increase the denseness of its structure. It is known that the critical radius of the surface nucleus $r_c$ depends on the overpotential value as follows: $r_c = s/ze\eta$, where $\eta$ is the overpotential; $s$ is the area occupied by one atom on the surface of the nucleus; $\varepsilon$ is the edge energy; $z$ is the transference electron numbers in a certain electrode reaction; and $e$ equals $1.062 \times 10^{-19}$ C. The surface morphologies of the electrodeposited Au layer are shown in Fig. 2a–d. The electrodeposition tests of Au were performed with different current densities by passing the same charge density (0.5 C cm$^{-2}$). To exclude the thickness effects of the Au layers obtained from the electrodeposition, all Au layers were prepared with same thickness (0.5 μm). The Cu substrate was fully covered by the electrodeposited Au layer, and a smaller crystalline grain size of Au was observed as the cathodic current density increased. However, a powdery and dendritic morphology, which is generally obtained at a high cathodic current and is well known as a mechanically weak structure, was formed at a current density of 10 mA cm$^{-2}$. Although the higher nucleation rate and smaller nuclei size can improve the mechanical properties and density of the electrodeposited layer, the applied current for electrodeposition should not exceed the critical current density to avoid the formation of a powder-like structure. From the current efficiency curve of electrodeposition conducted at a specific applied current, the efficiency gradually increased as the applied current density increased (1–5 mA cm$^{-2}$) and suddenly dropped to

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**Fig. 1** (a and b) Surface and (c and d) cross-sectional morphologies of PCB current collectors coated by Au electroless deposition. The inset of (a) is a photograph of the PCB current collector; (e) photograph and (f) surface morphology of the PCB current collector after the cell test.

**Fig. 2** Surface morphologies of the electrodeposited Au layers obtained with different current densities at a total charge of 0.5 C cm$^{-2}$: (a) 1 mA/cm$^2$, (b) 3 mA/cm$^2$, (c) 5 mA/cm$^2$, (d) 10 mA/cm$^2$; (e) current efficiency curve and (f) X-ray diffraction patterns of the electrodeposited Au layers obtained with different current densities at a total charge of 0.5 C cm$^{-2}$.
60.3% at 10 mA cm\(^{-2}\) (Fig. 2e). This trend was also confirmed from the XRD results (Fig. 2f). Two peaks located at 38.2° and 44.3° corresponded to the (111) and (200) planes of the crystalline Au phase (JCPDS no. 65-2870), respectively, and a peak located at 50.5° corresponded to the (200) plane of the crystalline Cu phase (JCPDS no. 85-1326). The peak density of Au (200) increased as the applied current density increased from 1 to 5 mA cm\(^{-2}\). However, the peak density of Au (200) suddenly decreased in the case of 10 mA cm\(^{-2}\), indicating insufficient deposition on the surface.

In addition to the constant current electrodeposition of Au, we conducted pulse electrodeposition by periodically applying a high cathodic potential and pausing the application of the potential with a specific time ratio (\(T_{\text{on}}\) and \(T_{\text{off}}\)) to increase the nucleation rate and decrease the nuclei size (Fig. 3a). Compared with the application of a constant current, rapid electrodeposition at a high cathodic peak potential (\(V_p\)) for \(T_{\text{on}}\) can significantly increase the nucleation rate, and the rest time for \(T_{\text{off}}\) allows the diffusion of Au ions to the electrochemical double layer. The \(T_{\text{off}}\) region can effectively prevent the deficiency of the Au ion reactant after the prior electrodeposition during \(T_{\text{on}}\).

To examine the corrosion resistance of the Au coating layers prepared under different electrodeposition conditions, we conducted potentiodynamic polarization tests in a 3 M methanol and 1 M H\(_2\)SO\(_4\) solution with voltage ranging from 300 to 1600 mV at room temperature (Fig. 4). Fig. 4a shows the polarization curves of the electrodeposited samples with different applied current densities (1–5 mA cm\(^{-2}\)), and the samples were compared with the sample with the electroless-deposited Au layer. As the electrode potential increased, the samples prepared by electrodeposition showed consistent current densities as a function of the corrosion rate above approximately 250 mV, corresponding to the passive region of the Au coating layer against the increasing electrode potential (oxidation power) in an acidic solution environment. The current density values of the samples decreased with increasing electrodeposition currents. The compact and highly nucleated Au coating layer can improve corrosion resistance against the harsh oxidation voltage and acidic environment. The Au coating layer electrodeposited at 5 mA cm\(^{-2}\) showed a lower current density value (1 mA cm\(^{-2}\) at 1000 mV in polarization curve). However, with an increasing electrode potential of the electroless Au coating sample, a sudden increase of current density up to 0.1 A cm\(^{-2}\) was revealed without a passivation region. This result indicates that the Au-coated sample prepared by electroless deposition did not sufficiently prevent severe corrosion,

Fig. 3  (a) Schematic time vs. applied voltage diagram of pulse electrodeposition; surface morphologies of the Au layers obtained by pulse electrodeposition at different peak potentials, (b) 1 V, (c) 1.5 V, and (d) 2 V.

**Fig. 4** Anodic polarization curves of the Au-coated PCB current collectors prepared by (a) constant current electrodeposition conducted with different current densities and (b) pulse electrodeposition conducted with different peak potentials. The anodic polarization tests were performed in a 3 M methanol and 1 M H\(_2\)SO\(_4\) solution at room temperature.
which is consistent with the morphology observations after the cell test (Fig. 1). Many defects along with the weak mechanical strength of the electroless-deposited Au layer cause the deterioration of long-term stability. As shown in Fig. 4b, pulse electrodeposition was also performed to promote the nucleation rate and to create smaller nuclei. The corrosion rate as a function of the average current density above 250 mV in the polarization curves was significantly reduced by the introduction of the pulse electrodeposition compared with electroless deposition and constant current electrodeposition. A higher peak potential (1 V → 1.5 V) for pulse electrodeposition exhibited better corrosion resistance of the Au coating layer.

The optimized PCB substrate employing a Au coating layer, which was prepared by pulse electrodeposition with a peak potential of 1.5 V, was evaluated as a current collector (Fig. 5). Fig. 5a shows the time course cell power profiles of current collectors employing pulse-deposited and electroless-deposited Au layers. The average cell power of the current collector with the pulse-deposited Au layer (700–750 mW, 23–25 mW cm$^{-2}$) was higher than that of the current collector with the electroless-deposited Au layer (670–720 mW, 22–24 mW cm$^{-2}$). This result implied that a current collector with a highly durable Au coating layer could enhance cell performance. Finally, cross-section morphologies of the pulse-deposited and electroless-deposited Au layers are shown in Fig. 5b and c. Although a peeled Au layer was found in the case of the electroless-deposited Au layer, a relatively dense coating was observed for the pulse-deposited Au layer. The dense structure achieved by high nucleation kinetics effectively prevented the unexpected generation of defects on the surface and enhanced the durability of the coating layer against harsh environments. A high resistive current collector employing the optimized Au coating layer can be expected to improve the long-term stability and performance of electronic and electrochemical devices.

**Conclusions**

In conclusion, the improved durability of the current collector was achieved by manipulating the Au coating layer on the PCB substrate using the electrochemical deposition method. We found that the Au coating layer prepared by electroless deposition showed surface defects, such as pinholes, and insufficient covering with weak mechanical strength. The durability of the Au coating layer was significantly enhanced using the electrodeposition method, and the corrosion resistance of the electrodeposited Au layer was optimized by the applied current densities during the constant current electrodeposition of Au. In addition, the introduction of the pulse electrodeposition method for the Au coating was more effective than constant current electrodeposition due to the higher nucleation rate and smaller nuclei size, corresponding to better covering properties and denser coating features. Finally, the PCB current collector employing the optimized Au layer created by pulse deposition exhibited a higher cell power performance compared with the current collector prepared by electroless deposition.

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**References**