Disposable Copper-Based Electrochemical Sensor for Anodic Stripping Voltammetry

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Stability of Cu/CuCl$_2$ RE vs. commercial Ag/AgCl RE. To access stability of the Cu/CuCl$_2$ RE, we examined the open circuit potential against a commercially-available double-junction Ag/AgCl RE (MI-401F, Microelectrodes Inc.) in saturated KCl solution (4.6 M at 20 °C) to accelerate electrode aging.[1] As results in Fig. S-1 show, the electrode potential drifted rapidly for the first few minutes, but "stabilized" at approximately -338 mV after 10 min with a slower drift rate of ~0.3 mV/min. The drift of the Cu/CuCl$_2$ RE is quite large compared to other microscale Ag/AgCl RE electrodes reported in literature,[2, 3] which exhibit an extremely low drift rate of ~0.034 mV/h, or <1 mV for longer than 100 h. Yet, the difference in such an aging experiment is expected since RE in that work was protected by multiple layers of membrane, while our RE is naked and directly exposed to the solution, which is simpler to fabricate and is an advantage from the device fabrication and reproducibility points of view. Other REs made of Ag/AgCl without protective layers also exhibited small potential drift of ~2 mV for at least 1000 min,[4] but the fabrication procedures, materials and electrode structure differ from ours in very significant aspects. Thus, additional comparison of the Cu/CuCl$_2$ and Ag/AgCl REs in our sensor is needed before a conclusion can be reached.
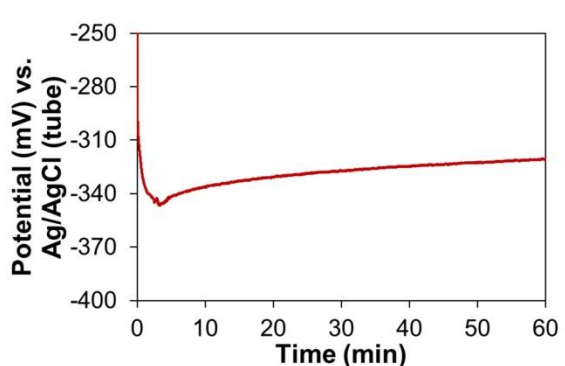

Fig. S-1. Stability of Cu/CuCl$_2$ as a reference electrode: the open circuit potential of Cu/CuCl$_2$ electrode in saturated KCl (buffered, pH 7.0) vs. commercial Ag/AgCl (double junction).

Optimization of stripping parameters. Before we demonstrated determination of Zn, experimental parameters (buffer pH, preconcentration potential and time,) and stripping waveform parameters were optimized for maximum stripping peak current and peak sharpness using 100 µL samples containing 10 µM of Zn in acetate buffer (0.1 M). For each parameter, experiments were performed in triplicate. For pH optimization, ASV was performed in acetate buffer with pH in the 4.65-6.5 range (Fig. S-2a). For pH < 6, reduction of water started at -0.9 V, which was close to the Zn peak at -0.8V. Acetate buffer with pH 6.5 provided the widest potential window in CV, while in ASV multiple peaks were observed as Zn hydroxides began to form at a nearly-neutral pH. Voltammograms at pH 6 showed the most stable peaks, with coefficient of variation = 12%, compared with 21%-75% for other pH values. Thus, pH 6 was identified as best.

Optimization of preconcentration parameters. Preconcentration potential is a critical parameter for ASV, thus different potentials from -0.9 to -1.3 V were tested to select the most suitable value (Fig. S-2b). When the potential was too negative, the formation of hydrogen from water reduction reduced efficiency of deposition and affected repeatability of experiments. ASV with preconcentration potential of -1 V provided both the largest peak current and the smallest variation, and was thus selected as the optimal deposition potential.

Preconcentration time is another critical parameter for ASV as it directly influences the sensor limit of detection and the overall time of analysis. Preconcentration times in the 1-10 min range were investigated (Fig. S-2c). For relatively short depositions, the Zn peak amplitude steadily increased with longer preconcentration time, saturating at 5 min. Additionally, the coefficient of variation for the 5 min preconcentration was 6%, but increased to 24% for the 10 min preconcentration, due to the partial degradation of the AE of Cu-based sensor. Thus, 5 min
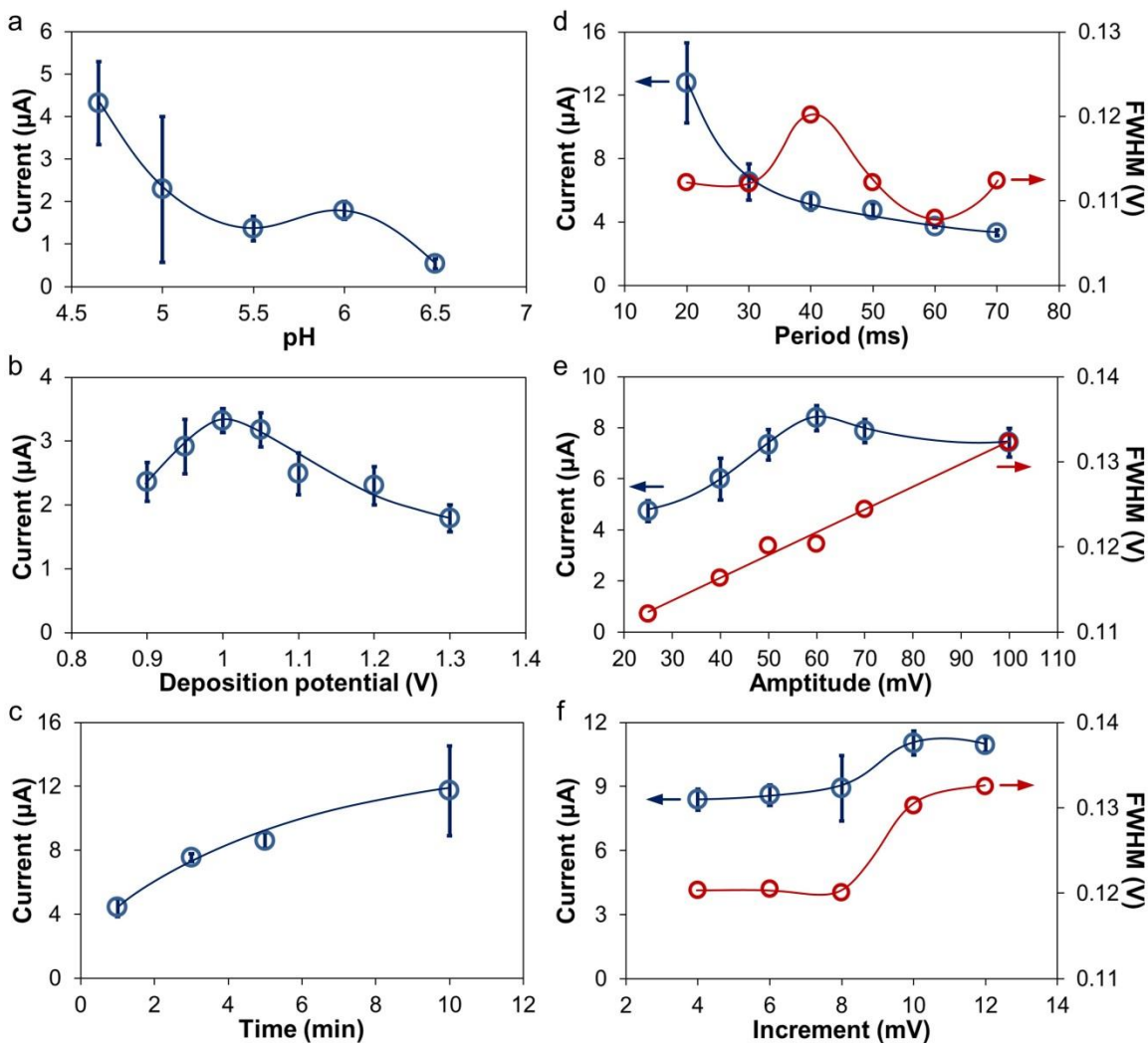
Fig. S-2. Optimization of experimental parameters: (a) pH of acetate buffer, (b) preconcentration potential, (c) preconcentration time, (d) square wave period, (e) square wave amplitude, (f) square wave increment. ASV performed in 10 µM Zn acetate buffer (0.1 M, 100 µL sample volume).

preconcentration time was selected for the following ASV experiments.

Optimization of waveform parameters. The waveform parameters of ASV using

Osteryoung square wave voltammetry for the stripping step were also optimized as shown in Fig.

S-2d-f. By decreasing the period and increasing amplitude and increment of the square wave,

the peak current kept increasing. However, the purpose of optimization was not only to increase

peak current which represents high sensitivity, but also to accomplish sharp peaks for the

accurate measurement of different metals in mixtures, and to reduce the device-to-device

variation to obtain low LOD. Therefore, another characteristic - full width at half maximum

(FWHM) - was also considered as a secondary factor to distinguish peak sharpness

straightforwardly and select the proper parameters. The larger FWHM indicates the peak begins

to lose its resolution even though its peak current is increasing, which increases the LOD, and

makes it challenging to quantify certain metals if their peaks overlap. Therefore, instead of using

extreme parameters for the square wave just to increase the peak amplitude, we carefully

optimized the values to achieve higher sharpness and resolution of the peaks. We selected 50 ms,

60 mV and 6 mV for period, amplitude and increment values, respectively, and the resulting

signal current was amplified from 3 µA when using default parameters of 70 ms, 25 mV and 4

mV, respectively, to 8 µA.

References

(1) Suzuki, H.; Hirakawa, T.; Sasaki, S.; Karube, I. *Sens. Actuators B: Chem.* **1998**, *46*, 146-154.

(2) Matsumoto, T.; Ohashi, A.; Ito, N. *Anal.Chim.Acta.* **2002**, *462*, 253-259.

(3) Suzuki, H.; Shiroishi, H.; Sasaki, S.; Karube, I. *Anal.Chem.* **1999**, *71*, 5069-5075.

(4) Polk, B. J.; Stelzenmuller, A.; Mijares, G.; MacCrehan, W.; Gaitan, M. *Sens. Actuators B: Chem.* **2006**, *114*, 239-247.