

# RENEWABLE SOLID ELECTRODES IN MICROFLUIDICS: RECOVERING THE ELECTROCHEMICAL ACTIVITY WITHOUT TREATING THE SURFACE

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**Abstract:** *we herein show for the first time a reproducible method for renewing solid electrodes whenever their surfaces are non-specifically changed without any surface treatment. These renewable electrodes are the closest analogue to the mercury drop electrodes. Our approach was applied in microfluidics, where the downsides related to contaminations of the electrode are more critical. The renewal consisted in manually sliding metal-coated microwires across a channel with the sample. For this purpose, the chip was composed of a single piece of polydimethylsiloxane (PDMS) with three parallel microchannels interconnected to one perpendicular and top channel to pump sample. The microwires were inserted in each one of the parallel microchannels acting as working, counter, and quasi-reference electrodes for voltammetry. This assembly allowed the renewal of all the three electrodes by simply pulling the microwires. The absence of any interfaces in the chips and the elastomeric nature of the PDMS allowed us to pull the microwires without the occurrence of leakages for the electrode channels even at harsh flow rates of up to 40.0 mL min<sup>-1</sup>. We expect this paper can assist the researchers to develop new microfluidic platforms that eliminate any steps of electrode cleaning, thus representing a powerful alternative for precise and robust analyses to real samples.*

**Keywords:** Microdevice; PDMS; Cleaning; Electroanalytical chemistry; Voltammetry.

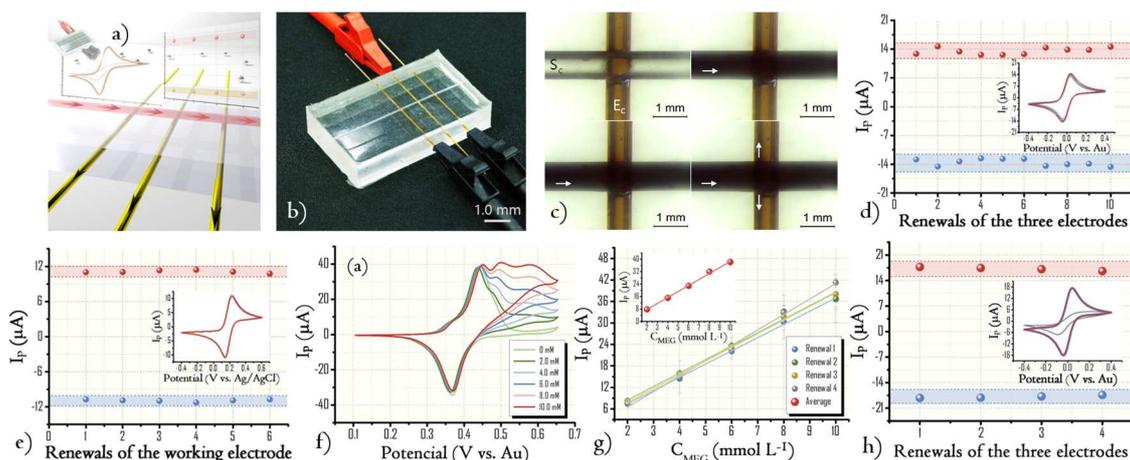
**Introduction:** the contamination, passivation, or fouling of the electrodes is a serious problem undermining the analytical performance of electroanalytical devices. The methods used to regenerate the electrochemical activity of solid electrodes involve mechanical, physical, or chemical surface treatments. To regenerate these electrodes with reproducible surface area is a challenge. Such reproducibility is crucial by eliminating further calibration steps in analytical experiments. Furthermore, the foregoing regeneration methods generally add operational time, complexity, chemicals, and instruments to the analysis routine. The electrochemical activity recovery is especially difficult in microfluidics because of two reasons. First, the electrodes are commonly placed inside irreversibly bonded chips. Second, such electrodes often rely on films with thicknesses ranging from tens of  $\mu\text{m}$  to 250 nm. Both of these aspects hinder more vigorous cleaning procedures such as polishing. Taking into account the relevance of the electrochemical detectors in microfluidics and the previously stated drawbacks associated to the contamination of solid electrodes (especially when integrated into microchannel), we herein show the creation of renewable solid electrodes in polydimethylsiloxane (PDMS) microfluidic chips. The electroactive area of microwire-based electrodes was reproducibly renewed without any surface treatment.<sup>1</sup> Thus, our approach could be considered as the closest analogue to the mercury drop electrode. To our knowledge, this is the first report on describing the deployment of renewable solid-state electrodes assuming the absence of electrode treatment.

**Experimental:** the renewal consisted of manually sliding metal-coated microwires across a perpendicular microchannel containing the sample. For this purpose, the devices (**Fig. 1(a,b)**) were composed of a single piece of PDMS with three parallel channels interconnected to one perpendicular and top channel (sample channel). Three metal-coated wires were mechanically inserted in each one of the parallel channels acting as working (WE), auxiliary (AE), and quasi-reference (QRE) electrodes. This setup allowed us renewing the electrochemical activity of all the three electrodes simply pulling the wires. The chips were fabricated by the bondless method that relied on sequential steps of polymerization and scaffold removal (PSR).<sup>1</sup> The electrodes consisted of thin-films deposited on stainless steel microwires (720- $\mu\text{m}$  diameter) by electron beam vapor deposition. AE was composed of Cr/Au films (150 nm). Cr/Au or Cr/Ag films (200 nm) were used as reference electrodes (coated with AgCl), whereas Cr/Au or Cr/Ni (300 nm) films acted as WE. The solutions were moved by a syringe-pump.

The reproducibility of the renewal was initially investigated by assessing the values of peak current obtained for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple in cyclic voltammetry. The tests were realized to new surfaces pulling either only the working electrodes or the three electrodes. For renewal into the microfluidic channel, the wires were pulled in the presence of the sample in the channel after a sequence of measurements ( $n = 3$ ). WEs coated by Au and solutions of 10.0 mmol L<sup>-1</sup>  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 100.0 mmol L<sup>-1</sup> KCl were used. The potential range changed of -0.40 up to +0.40 V with scan rate ( $v$ ) of 0.05 V s<sup>-1</sup>. Cr/Au or Cr/Ag/AgCl films acted as reference electrodes.

The renewal reproducibility was also tested using cyclic voltammetry to monoethylene glycol (MEG). Ni-based WE and MEG solutions prepared in NaOH and Na<sub>2</sub>SO<sub>4</sub> at 100.0 mmol L<sup>-1</sup> were employed. The potential range was of +0.10 up to +0.65 V with  $v$  of 0.05 V s<sup>-1</sup>. Analytical curves (2.0 to 10.0 mmol L<sup>-1</sup> of MEG,  $n = 5$ ) were constructed for each surface of Ni. Only WE was renewed. The analytical sensitivity obtained for the diverse curves were used to evaluate the renewal performance. To analyze MEG, the Ni WE surface was in-situ modified with Ni(OH)<sub>2</sub> nanoparticles (125  $\pm$  8 nm) as detailed in literature.<sup>1,2</sup> Herein, we employed Cr/Au as QRE.

Finally, we further assessed the renewal pulling three Au-coated microwires after in-situ passivation of the electrodes with 50.0 mmol L<sup>-1</sup> 1-octadecanethiol in ethanol for 1 h. The peak currents recorded for 10.0 mmol



**Fig. 1.** Renewable solid electrodes in microfluidics. Image generically showing the concept of the method (a), chip with the electrodes (b), stereoscopy images of the channels (c), renewal reproducibility data by analyzing  $\text{Fe}(\text{CN})_6^{3-/4-}$  utilizing Cr/Au (d) and Cr/Ag/AgCl films (e) as reference electrodes, voltammograms to MEG standards (f), analytical curves to MEG on four renewed surfaces of WE (g), and reproducibility data by analyzing  $\text{Fe}(\text{CN})_6^{3-/4-}$  after passivating WE with thiol (h). In (c), the fluid leaked from sample channel (S<sub>c</sub>) to electrode channel (E<sub>c</sub>) just at a flow rate of 45.0 mL min<sup>-1</sup> as indicated by the white arrows (last image). In (d) and (e), the voltammograms for oxidation and reduction of  $\text{Fe}(\text{CN})_6^{3-/4-}$  are shown as insets. In (g), the inset illustrates the curve constructed from the global averages of the signals of all the renewals. In (h), the voltammograms in red and gray were recorded for the same surfaces before and after exposing the electrodes to thiol, respectively. The blue voltammogram (similar to the red) was obtained after the subsequent passivation and renewal of the electrodes. In (d,e,h), the areas in red and blue represent the limits calculated through the Student's t test. I<sub>p</sub>, peak current; I, current; and C<sub>MEG</sub>, concentration of MEG standard.

L<sup>-1</sup>  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 100.0 mmol L<sup>-1</sup> KCl were used again to study the renewal reproducibility. The experimental conditions were the same in relation to those described above to the Au working electrodes.

**Results and discussion:** the walls of the electrode ( $671 \pm 3 \mu\text{m}$ ) and sample ( $795 \pm 6 \mu\text{m}$ ) channels showed well-defined edges and low roughness (Fig. 1(c)). The microwire/channel ratio of 1.1 was great by ensuring an easy manual sliding of the electrodes and avoiding leakages even at harsh flow rates of up to 40.0 mL min<sup>-1</sup>. The reproducibility of the electrochemical recovery when using  $\text{Fe}(\text{CN})_6^{3-/4-}$  as redox couple was satisfactory in all the cases (Fig. 1(d,e)). The best data were obtained when Ag/AgCl was used as reference electrode. In this case, the global averages of the peak currents for  $\text{Fe}(\text{CN})_6^{3-/4-}$  oxidation and reduction were  $11.1 \pm 0.2 \mu\text{A}$  and  $10.9 \pm 0.2 \mu\text{A}$  ( $n = 18$ ), respectively. The RSDs were only 2.1% for oxidation and 1.8% for reduction. The confidence intervals ranged from 0.1 to 0.3  $\mu\text{A}$ . With regard to the test involving analytical curves for MEG (Fig. 1(f,g)), the renewal processes showed a satisfactory reproducibility again. Considering the four curves, the analytical sensibilities exhibited a global average of  $3.8 \pm 0.1 \mu\text{A mmol}^{-1} \text{L}$  ( $n = 4$ ) with a RSD of 3.5%. The analyte contents obtained by the four renewals pulling only the working electrode would be reproducible according to Student's t tests at 95% confidence level. For a response of 24  $\mu\text{A}$ , e.g., the MEG amounts determined by the curves would show an average of  $6.3 \pm 0.2 \text{ mmol L}^{-1}$  ( $n = 4$ ). In terms of the RSD, its value would be only 3.1%. For the evaluation of the renewal after passivating the electrodes (Fig. 1(h)), the peak currents to  $\text{Fe}(\text{CN})_6^{3-/4-}$  after the thiol passivation were reduced to roughly 80% compared with the initial currents. This data was because the increase in the resistance to electron transfers. Otherwise, the electrochemical activity was effectively and reproducibly recovered by pulling all of the three electrode according to Student's t tests at a confidence level of 95%. The global averages of the peak currents were  $17.2 \pm 0.5 \mu\text{A}$  (oxidation) and  $17.9 \pm 0.4 \mu\text{A}$  (reduction) ( $n = 12$ ). The RSDs were 2.8% for oxidation and 2.1% for reduction. In relation to the intra-assay precision, the confidence intervals for the same surface changed of 0.2 up to 0.6  $\mu\text{A}$  only.

**Conclusion:** renewable solid electrodes are, to the best of our knowledge, described for the first time assuming the absence of any surface treatment. This process offers reproducibly recovering the electrochemical activity of the working, reference, and counter electrodes. The renewal relied on simply pulling metal film-coated microwires across a top channel containing the sample. The electrochemical activity regeneration herein shown eliminates the necessity for constructing new analytical curves in order to achieve reproducible results of analyte concentration. Furthermore, the absence of any interfaces in the chips and the elastomeric nature of the PDMS allowed us to easily pull the wires without leakage in the electrode channels even at a flow rate of 40 mL min<sup>-1</sup>. A paper about the results herein discussed was recently published in 'Analytical Chemistry'.<sup>1</sup>

#### References:

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