



Facile and versatile approaches to enhancing electrochemical performance of screen printed electrodes

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ABSTRACT

Screen printed carbon electrodes provide attractive opportunity for the development of miniaturized low cost electrochemical sensors. However, the electrodes display very low level of electrochemical performance due to the nonelectroactive components in the ink formulation and relatively low graphitic carbon content imposed by the constraints of screen-printing. In this work, selective etching action of a judiciously selected organic solvent was envisaged to improve the electrochemical characteristics of the electrodes. The procedure involves soaking the electrode strips in N,N-dimethylformamide (DMF) for just minutes of etching followed by drying. Five minutes DMF treated electrode, for instance, showed a 100-fold increase in the heterogeneous charge transfer kinetics compared to the untreated electrodes. The effective area of the solvent treated electrode was 57-fold of its apparent geometric area. The solvent treated electrodes also showed a dramatically decreased charge transfer resistance from ca. 18,000 Ω to 180 Ω . The results of surface examination using scanning probe microscopy and electrochemical impedance spectroscopy revealed enhancement in the porosity of the solvent treated electrodes. The procedure is versatile and applicable to other screen-printed electrodes such as gold, silver or silver/silver chloride to improve the performances characteristics including stability. The ability to activate several electrodes simultaneously and multiple re-usability of the solvent makes this approach cost effective and very promising to facilitate mass production of miniaturized and disposable electrochemical sensors.

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1. Introduction

Disposable screen-printed carbon electrodes (SPCEs) fabricated via thick-film (screen-printing) technology offers the most promising route for the development of miniaturized sensors for the detection of different analytes including microorganisms [1,2], proteins [3–7], glucose [8–10], or nucleic acids [11,12], among others, in point-of-care testing and on-site monitoring. The low cost of the material (SPC) and its compatibility for mass production make SPCEs the primary choice for researchers and diagnostic companies, particularly for electrochemistry driven applications. The great interest in the SPCEs is also due to attractive features of the carbon: chemically inert, low background currents and wide potential window [13,14]. The performance of SPCEs, however, depends critically on the surface properties and the nature of the carbon ink. Due to the nonelectroactive additives in the inks and hence the

relatively low graphitic carbon content imposed by the constraints of screen-printing, the redox activity and the overall analytical performance of the electrodes are compromised [15,16]. The nonelectroactive components (or simply contaminants) including the polymeric binders in the ink block the electrochemically active graphitic particles leading to slower rates of heterogeneous charge transfer kinetics and seriously affect reversibility of electrochemical reactions at the electrodes. In addition to the impeding nature of the ink, commercial SPCEs exhibit wide range of electrochemical reactivities for benchmark redox systems. SPCEs from different commercial supplier display different background currents and have varying performance depending on the type of specific electrochemical techniques employed [15,17]. Such differences in the performance of the electrodes have been ascribed to variations in: (i) the graphitic loading, (ii) degree of electrochemical accessibility of the graphitic edges and (iii) the nature of the graphite particles and its functionalization [15]. These characteristics the electrodes, however, can be tuned using proper surface pretreatment methods.

The surface pretreatment methods for SPCE employed to-date including electrochemical, chemical treatments prior to electrochemical, and exposure to UV and oxygen plasma are usually based on either increasing the density of oxygenated groups on

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the electrode surface or increasing the exposure of the electroactive graphitic particles. Wang et al. [17] proposed a short electrochemical pre-anodization of the electrodes for improved electrochemical performance. Cui et al. [18] described pretreatment procedure in saturated Na_2CO_3 solution at 1.2 V as a mild and effective condition for improving the electrochemical performance of SPCE. Wei et al. [19] showed further improvement in the heterogeneous charge transfer rate constant and electrochemical reversibility by soaking fresh SPCEs into concentrated NaOH for tens to hundreds of minutes prior to pre-anodization in low concentration NaOH. Notwithstanding the enhancement in the electrode performance, NaOH treatment may have problem of detaching the SPCEs from the substrate [18]. Kostaki et al. reported the possibility to improve electrochemical characteristics of SPCEs based on galvanostatic treatment (5 μA for 6 min in 0.1 M H_2SO_4) [20]. Osborne et al. [21] described activation of SPCEs based on the use of UV light from an excimer laser source to selectively etch the organic binding polymer from the composite surface thereby exposing sublayers of carbon particulates. Wang et al. [22] reported the use of plasma treatment to increase the graphitic edge planes as effective mechanism to enhance the electrochemical performance of screen-printed electrodes. These activation procedures may enhance the performance of the electrodes, but may either require cost intensive instrumentation, or not suitable for mass production or introduce surface functionalities that may lead to loss of stability of the performance of the electrodes. Therefore, a simple, low cost and yet effective strategy for the activation of screen printed electrodes without compromising the stability is continuously being sought.

Here, we report a new approach to enhance the electrochemical performance of SPCEs via the mechanism of increasing graphitic loading and exposure of more pristine graphitic edges. SPCE is a typical composite material composed of graphite particles and organic resins as binding agents and other components for dispersion of the particles. Thus it was envisaged that, since not all the components can dissolve in a judiciously selected organic solvent, a controlled and selective etching of the SPCEs' surface can increase the graphitic loading and exposure of more pristine graphitic edges. Scanning probe microscopes and electrochemical methods were used to characterize surface morphology and enhancements in the area of the solvent treated electrodes as compared to the untreated electrodes. The electrochemical characteristics including charge transfer kinetics and reversibility at the solvent treated electrodes were studied using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. The experimental results strongly reinforced the proposed mechanism. This simple, low cost and yet effective surface pretreatment procedure is more generic and can be applied as a versatile approach to enhance the electrochemical characteristics of other screen printed electrodes such as screen printed gold, silver or silver/silver chloride given the composite nature of all the electrodes and the presence of such contaminants as binders or dispersion agents in all of the inks. The proposed mechanism, although follows novel approach, is consistent with the previous reports [21–27].

2. Experimental

2.1. Materials and equipments

All the chemicals including $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{Sr}(\text{NO}_3)_2$ and N,N-dimethylformamide (DMF) were obtained from Sigma Aldrich. Distilled and de-ionized water (PURELAB UHQ II, ELGA) was used throughout the study. The substrate for printing was a polyester (PET) film with a thickness of 175 μm provided by ThyssenKrupp Plastic Iberica S.A. (Spain). The screen-printing apparatus used was DEK-248 (DEK International) equipped with a

DEK Align 4 vision module (a two-point optical alignment system). The screen of a polyester mesh 305 (120/34), with an emulsion thickness of 13 μm was designed in-house and manufactured by DEK International (France). The squeegee used was made of polyurethane and provided by DEK International (model SQA152 with a contact angle of 45° and a hardness factor of 70). The inks (7102 conductor paste based on carbon and 5874 conductor paste based on Ag/AgCl) were provided by DuPont Ltd. (UK). Other conductor inks – C2030519P4 carbon/graphite and 26-9203 conductive carbon were obtained from Gwent and SunChemical, respectively. The oven used for curing/drying purposes was a Digi-heat 150 L oven provided by JP Selecta S.A., Spain.

2.2. Fabrication, surface pretreatment and characterization

The printing was performed according to the procedure reported previously by our group [28]. The thickness (7.5 μm) of the SPCE film was measured using a Mitutoyo SJ-301 profilometer and the data received were analyzed with the software SURFPAK-SJ Version 1.401 (Mitutoyo Messgerate GmbH, Japan). The plastics containing several screen-printed electrodes were placed vertically in a rectangular chromatographic chamber containing N,N-dimethylformamide for 5 min to expose all the electrodes entirely to the solvent. The solvent treated electrodes were then cured at 100 °C for 20 min in the oven. The surface area enhancement resulting from the solvent treatment was characterized using electrochemical methods (electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV)), environmental scanning electron microscopy (FEI model QUANTA 600 manufactured by FEI (USA)) and atomic force microscopy. The adhesive single-side coated with acrylic (Adhesive research; ARCARE8565) was patterned and machined with a Fenix Flyer CO_2 laser marker (Synrad) using 4 passes at 50% of power to produce a circular opening of radius = 1.5 mm which when pasted on the electrode surface delimits a constant geometric area of the electrode to be 7.07 mm^2 .

2.3. Electrochemical studies

Electrochemical studies involved a prior preparation of the solvent treated and untreated electrodes to delimit a constant area of the electrode surface as described in the previous section. The electrochemical performance of the solvent activated electrode surface of fixed area was investigated by recording cyclic voltammetry (CV) and EIS of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple. All the electrochemical measurements including EIS were recorded in a 2 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ solution containing, unless otherwise stated specifically, 0.1 M $\text{Sr}(\text{NO}_3)_2$. A one-compartment, three-electrode electrochemical cell consisting of SPCE (either solvent treated or untreated) of geometric area 7.07 mm^2 as working, screen printed Ag/AgCl electrode (of geometric area 7.07 mm^2) as reference and platinum electrode as counter were employed. All dc potentials (Edc) were referred to this reference electrode. A general purpose electrochemical system, the Autolab PGSTAT12 (Ecochemie) with frequency response analyzer (FRA2), was used. The impedance spectra were recorded in the 100 kHz–0.1 Hz frequency range. The amplitude for the sinusoidal excitation signal was 10 mV and the temperature was 20–23 °C. The spectra were then fitted to an equivalent electrical circuit model using the Autolab impedance analysis software.

3. Results and discussion

3.1. Microscopic characterization

Surface characteristics of composite electrode materials can be tuned effectively using solvents. Fig. 1(a) and (b) show the

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