Textile-based Electrochemical Sensing: Effect of Fabric Substrate and Detection of Nitroaromatic Explosives

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Abstract

This study examines the influence of textile substrates upon the behavior of wearable screen-printed electrodes and demonstrates the attractive sensing properties of these sensors towards the detection of nitroaromatic explosives. Compared to electrodes printed on common cotton or polyester substrates, GORE-TEX-based electrochemical sensors display reproducible background cyclic voltammograms, reflecting the excellent water-repellent properties of the GORE-TEX fabric. The wetting properties of different printed textile electrodes are elucidated using contact angle measurements. The influence of laundry washing and mechanical stress is explored. The GORE-TEX-based printed electrodes exhibit favorable detection of 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) explosives, including rapid detection of DNT vapor.

Keywords: Screen-printed electrodes, Wearable sensors, GORE-TEX, Explosive agents, Fabrics, Textile, Security

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1 Introduction

Wearable chemical sensors can provide useful information regarding the wearer’s health or for monitoring their surrounding environment [1,2]. Textiles represent an attractive class of substrates for fabricating such wearable chemical sensors [3,4]. Fabrics present many unique opportunities and advantages that can be exploited for various practical applications and are especially suited to handle the rigors of field-based use where durability and light-weight are core requirements [3,4]. The integration of chemical sensing into textiles thus permits the wearer to receive extremely valuable and timely information without compromising the functionality or comfort of the garment. Recently we reported on the fabrication of thick-film (screen-printed) amperometric sensors directly onto elastic waist of undergarments [5]. The study indicated that screen printing technology, which involves printing patterns of conductors and insulators on planar substrates, is extremely attractive for preparing such wearable electrochemical sensors. However, little is known about the compatibility of diverse varieties of fabrics with the thick-film sensor fabrication process. Textile-based sensing applications require a dense, hydrophobic outer surface with desirable morphology which can be realized by conventional screen-printing techniques.

The present study examines the influence of different textile materials upon the quality and performance of screen-printed electrodes (SPE) and demonstrates, for the first time, the ability of such printed textile sensors to detect explosive agents of importance in security applications. In particular, differences in the hydrophobicity of the textile substrate are shown to have a profound effect upon the behavior of the corresponding SPE. Textiles can be made from many sources: animal (wool), plant (cotton), or synthetic (nylon, polyester) that possess widely different structures and physical and chemical properties. The optimal textile candidate for supporting printable electrochemical sensors would possess inert properties and yield stable operation for extended periods of time under normal and heavy wear. Additionally, liquid-phase measurements require the utilization of water-proof fabrics, which would serve as excellent platforms for facilitating chemical reactions in vitro. The fabrics evaluated in the present study include cotton, polyester, and GORE-TEX, a widely used constituent of outdoor garments. GORE-TEX fabric, a textile known for its exceptional breathable and water-proof properties, is shown to be a very promising substrate for thick-film electrochemical sensors.

In addition to monitoring the wearer’s personal health, there are considerable demands for developing wearable sensors that monitor the wearer’s local environment in order to identify potential hazards and threats and thereby provide a further level of protection [6]. Monitoring the external environment can lead to increased survival of the wearer in hazardous conditions. For example, growing concerns regarding terrorist activity have gener-
ated tremendous demands for innovative field-portable tools capable of detecting explosive compounds in a faster, simpler, and reliable manner [7]. Electrochemical sensors offer unique opportunities for addressing the needs for field screening and identification of various explosives [8]. In particular, the inherent redox activity of the widely used nitroaromatic explosives (e.g., 2,4,6-trinitrotoluene, TNT) makes them ideal candidates for electrochemical detection [8,9]. As will be illustrated below, the new GORE-TEX SPE offers convenient detection of nitroaromatic explosives in the liquid- and gas-phases, and holds promise for monitoring hazardous situations.

2 Experimental

2.1 Chemicals and Materials

Potassium ferrocyanide and acetonitrile were obtained from Fisher Scientific (Pittsburgh, PA) and used without further purification. Potassium phosphate (both monobasic and dibasic), 2,4-dinitrotoluene (DNT), potassium chloride, and agarose 1-A were purchased from Sigma-Aldrich (St. Louis, MO). 2,4,6-trinitrotoluene (TNT) solution (1000 µg/mL in acetonitrile) was obtained from Cerilliant (Round Rock, TX). Deionized water (18 MΩ·cm) from a NANOpure Diamond system (Thermo Scientific Barnstead) was used to prepare all solutions. All electrochemical measurements were carried out using a 50 mM phosphate buffer solution (pH 7.4). The GORE-TEX (registered trademark of W.L. Gore & Associates, Inc., Flagstaff, AZ) fabric (3-ply Nylon woodland camouflage) was purchased from Rockywoods (Loveland, CO). Polyester and cotton fabrics (both 100%) were cut from garments that were purchased from the local department store.

2.2 Preparation of Sensing Electrodes

The fabrics were pre-heated at 130 °C for 1 hr before the printing process. A semi-automatic screen-printer (Model TF 100, MPM, Franklin, MA) was employed to print the electrodes through a patterned stencil. A silver/silver chloride ink (E2414, Ercon, Wareham, MA) was used to define the conductive under layer as well as the reference electrode. A carbon ink (E3449, Ercon, Wareham, MA) was then overlaid on the conductor to define the working and counter electrodes. Insulating ink (E6165, Ercon, Wareham, MA) was subsequently printed to define the electroactive area of the electrodes, followed by curing for 30 min at 125 °C. All tests and electrochemical measurements were performed after cutting the fabric into 10 x 34 mm strips containing the three-electrode set.

For the preparation of the vapor-phase fabric-based sensor, a polyester film coated with pressure-sensitive adhesive (ARcare 8259, Adhesives Research, Inc., Glen Rock, PA) with a 7 mm diameter opening was applied on the surface of the GORE-TEX fabric-based sensor (described above) to create a cavity for casting the solid electrolyte. A hydrogel electrolyte was prepared by dissolving 100 mg agarose into 5 mL potassium chloride solution (0.5 M) under stirring. The mixture was then brought to a boil (around 200 °C) and remained at this temperature for 5–10 min under continuous stirring until the agarose dissolved completely. Subsequently, the gel solution was cooled to 65 °C and kept at this temperature (with stirring applied) for the further use. The solid electrolyte of the sensor was cast by dipping the fabric-based sensor into the agarose solution and promptly removing the sensor, allowing the agarose to solidify on the electrode surface at room temperature.

2.3 Apparatus and Measurements

All electrochemical measurements were performed at room temperature using a CH Instruments 1232A Electrochemical Analyzer (Austin, TX). For the liquid-phase measurements, a 60 µL sample droplet was placed on the printed electrode surface. Both cyclic voltammetry (CV) and square-wave voltammetry (SWV) were used for evaluating the performance of the fabric-based sensors with the experimental parameters indicated in the individual figures. To investigate the wetting properties of electrodes printed on various fabrics, the CV scan was initiated immediately upon placing the sample drop onto the electrode surface. The five initial cycles of the CV were sampled for comparison. The steady-state CV was also recorded until the traces roughly overlapped for two consecutive cycles. Gas-phase measurements were performed by inserting the GORE-TEX fabric-based sensor into a 30 mL glass jar containing 60 mg DNT powder for 30 min. SWVs were recorded successively with increasing exposure time (namely the time period after the sensor’s insertion into the beaker containing DNT).

To examine the effect of bending upon the electrochemical/sensing abilities of the electrode, the bending operation was performed by the same individual and only applied on the electroactive section of electrodes. Each bending experiment consisted of the application of an inward 180° bend with a 1 mm bend radius for 1 s. Multiple bending was separated with 1 s release intervals. The laundry washing was performed using a Whirlpool (Benton Harbor, MI) washing machine. The washing process consisted of 8 min washing with detergent followed by 12 min rinsing with water and 3 min spinning. The morphology of the fabric-based sensor was examined using a field emission scanning electron microscope (Philips XL30, Amsterdam, The Netherlands). All specimens were coated with chromium prior to analysis using a sputtering instrument (Energy Beam Sciences Emitech K575X, East Granby, CT). A deposition current of 130 mA was applied for 30 s to coat ~15 nm of chromium on the sample surface. The contact angles of water on different fabrics were measured using a Goniometer (CAM 100, KSV, Helsinki, Finland). A micro syringe (10 µL) was used to cast the water drop on the surface. Side view images were captured and the contact angles were deter-
mined by the instrument (by fitting the captured drop shape to the shape calculated from the Young–Laplace equation). Measurements were performed at ambient temperature (25°C) in air and repeated at least 5 times on the fresh surfaces.

3 Results and Discussions

Screen-printing technology has recently been leveraged to fabricate sensing electrodes on the elastic waistband of undergarments [5], in connection with the detection of important electroactive substances such as hydrogen peroxide (H₂O₂) and reduced β-nicotinamide adenine dinucleotide (NADH). Such printed textile electrodes exhibited favorable electrochemical behavior and mechanical or adhesion properties, although the textile absorbed the sample solution due to its hydrophilic nature, leading to deteriorated sensing ability over time. A fabric possessing water-repellant properties and a densely-woven structure would serve as an excellent candidate for use as the substrate to enable stable operation. It is thus important to examine different types of textiles as potential substrates for wearable screen-printed electrochemical sensors.

We evaluated two types of widely-available fabric materials, 100% polyester and 100% cotton, as well as GORE-TEX, a completely waterproof and breathable fabric intended for outerwear. The wettability of the substrate is often characterized by measuring the dynamic contact angle formed between a liquid drop (water) and a solid surface. Wetting is favored by low interfacial, high solid surface and low liquid surface free energies. In fact, such wettability is arbitrated by composition, pore size, surface structure and porosity of the fabric. Figure 1A compares optical images captured in real-time contact angle measurements on (i) GORE-TEX, (ii) 100% polyester, (iii) 100% cotton, and (iv) 35% cotton + 65% polyester at 0 (left) and 1.5 s (right) following placement of a 10 μL water droplet on the fabric’s surface. These images indicate that at the elapsed time of 1.5 s, the GORE-TEX surface did not wet, whereas the droplets were almost entirely absorbed by the three other fabrics: 100% polyester, 100% cotton, and 35% cotton + 65% polyester blend. Apparently, the GORE-TEX fabric exhibited the greatest hydrophobicity among all the textiles examined.

Further, apparent contact angle, θ, for each fabric was evaluated using a Goniometer. Since a polar liquid probe like water penetrates rapidly through the hydrophilic matrices ((ii) 100% polyester, (iii) 100% cotton, and (iv) 35% cotton + 65% polyester), the measurement of contact angles between such probes is not feasible. The attractive hydrophobicity/hydrophobicity of GORE-TEX is indicated from an inspection of the contact angle measurement shown in Figure 1B. The contact angle was found to be 130°±5°. The distribution of the fluorine atom around the carbon polymer backbone in GORE-TEX has low surface energy which makes it non-polar. A strong surface tension is formed due to this difference in the surface energy between the water droplet and GORE-TEX membrane. As a result, water beads form...
and the textile exhibits hydrophobic properties. It is important to note that the resistance to wetting observed on the GORE-TEX fabric corresponds to the waterproof property claimed by the manufacturer. The pores of GORE-TEX membranes are smaller (by several orders of magnitude) than the individual water droplets [10]. As the wetting rate exhibited by the other fabrics was quite rapid, the effect of wetting on the electrochemical behavior was evaluated further.

To further characterize the effect of wetting upon the electrochemical sensing performance, cyclic voltammetry was performed using various fabric-based electrodes. Figure 2 shows the repetitive cyclic voltammograms (CVs) recorded using the GORE-TEX (A), 100% polyester (B), and 100% cotton (C) fabric-based electrodes in both phosphate buffer (i) and 10 mM potassium ferrocyanide solution (ii). To examine the dynamic transition of the wetting condition, repetitive CV experiments were conducted with a relatively high scan rate (300 mV s\(^{-1}\)). With respect to the background measurements (in phosphate buffer), the GORE-TEX fabric-based electrode exhibited minimal changes in the current upon repetitive scans. As the number of scanning cycles increased, a significant increase in the recorded current is observed for both the 100% polyester and 100% cotton fabric-based electrodes (particularly at potentials greater than 0.4 V). This can be ascribed to an increase in the active electrode area owing to the wetting effect. The wetting transition is also confirmed by observation whereby the entire fabric-based electrode strip was eventually wetted by the sample solution. A similar behavior also occurred in the ferrocyanide solution (ii) where the GORE-TEX fabric-based electrode possessed highly consistent CVs between subsequent cycles. On the other hand, a continually increasing current is observed in both 100% polyester and 100% cotton fabric-based electrodes over the duration of the experiment. It is important to note that the GORE-TEX fabric-based electrode yielded comparable redox properties as traditional carbon printed electrodes on inert solid substrates. However, only oxidation peaks at 0.4 and 0.24 V are recognizable in the 100% polyester and 100% cotton fabrics, respectively, whereas the reduction peaks are largely obscured. These results demonstrate the attractive electrochemical properties of the GORE-TEX fabric-based electrode. All subsequent analytical work was thus carried out with the GORE-TEX sensor.

The GORE-TEX fabric-based sensor is depicted in Figure 3A. Figure 3A (left) shows an array of eight printed carbon disk working electrodes, as well as one counter (carbon) electrode and one reference (Ag/AgCl) electrode. Each sensor was insulated by printing an insulting ink around the active electrode area, thereby forming the complete GORE-TEX fabric-based electrode array (Figure 3A middle). In addition, a typical three-electrode design is patterned on the GORE-TEX substrate (Figure 3A right), which is used in this study. The surface roughness and heterogeneous nature of the carbon layer is expected to affect the electrochemical behavior and hence it becomes essential to study the morphology of such surfaces. Micrographs of the surface morphology, the boundary of the printed carbon electrode, and a close-up of the printed carbon electrode surface on the GORE-TEX substrate are displayed in Figure 3Bi, ii, and iii, respectively. Figure 3Bi depicts the typical morphology of woven nylon protective layer employed in GORE-TEX

![Fig. 2. Cyclic voltammograms of various fabric-based sensing devices in (i) 50 mM phosphate buffer (pH 7.4) and (ii) 10 mM potassium ferrocyanide. First five initial scanning cycles are shown. Fabrics: (A) GORE-TEX, (B) 100% polyester, and (C) 100% cotton. Scan rate, 300 mV s\(^{-1}\).](image-url)
fabric. An SEM image in Figure 3Bii illustrates the grainy carbon layer, uniformly coated over the substrate. Note that the carbon electrode printed on the woven nylon fabric possessed a well-defined appearance with relatively smooth conductor edges, as opposed to printed electrodes on polyester and cotton fabrics where the fiber structure is less organized, which served to hamper the printing of the carbon electrodes (not shown). No apparent defects or cracks are observed (ii and iii), which demonstrates the regularity of the printed electrodes on each fiber. A further magnified image of the carbon electrode is shown in Figure 3Biii and illustrates the surface morphology in greater detail. The carbon layer possesses a non-porous surface and consists of two different sized carbon particles (3 μm and <1 μm diameters) embedded in the binder matrix.

Although GORE-TEX-based textiles are known to be less stretchable and more robust than other fabrics, normal wear and upkeep may affect the microstructure and morphology of the GORE-TEX fabric-based sensor and hence its performance. The influence of such mechanical stress thus requires a detailed examination. The GORE-TEX fabric-based printed electrodes were thus subjected to successive bending operations and the influence of this mechanical stress upon the electrochemical performance was examined. Employing 10 mM potassium ferrocyanide as the analyte, CVs were obtained after repeated bending of the fabric substrate (up to 60 bending operations). A CV was recorded after every 10 bends. As illustrated in Figure 4A, such repeated bending of the substrate did not have a detrimental affect on the voltammetric response. Figure 4B reveals the current profiles recorded from the redox current of ferrocyanide whereby the effect of this prolonged bending operation is minimal.

While our early effort was aimed at monitoring the wearer’s health [5], wearable textile sensors may also be used to monitor the wearer’s surrounding environment. For example, textile-based printed electrodes may enable the sensitive detection of explosive compounds hence providing an easily-deployable tool, particularly in security and military applications. Inline with the goal of assessing the levels of DNT and TNT in the environment, the performance of the GORE-TEX fabric-based sensor was evaluated by employing a hypothetical analytical procedure that one could perform in the field (i.e. placing a drop of a liquid under test on a fabric-based sensor). Figure 5 illustrates the square-wave voltammograms (SWVs) of the GORE-TEX fabric-based sensors for increasing levels of DNT (A) and TNT (B) over the 0 to 50 μg/mL range. In direct comparison with reported results in the literature [11,12], the GORE-TEX fabric-based sensor exhibited a well-defined peak at −0.86 V for DNT and two reduction peaks (at −0.75 and −0.95 V) for TNT. Note also the appearance of a second reduction signal (around −1.02 V) at higher DNT concentrations. For both nitroaromatic explosives, the first peak corresponds to the reduction of the nitro groups, whereas the second peak corresponds to the reduction of the hydroxylamine product to an amine one. Owing to the relatively significant signal at the less negative potential, calibration curves were plotted correlating the current signals at −0.86 V (Figure 5A) and −0.75 V (Figure 5B) with the
explosive concentration. These display high linearity ($R^2 > 0.99$) along with highly sensitive detection of DNT (0.38 µA mL µg$^{-1}$) and TNT (0.33 µA mL µg$^{-1}$). For both DNT and TNT, a low detection limit of around 1 µg/mL can be estimated from the concentration given a signal equal to the blank signal ($y_B$) (intercept) plus three standard deviations of $y$-residuals ($s_y$). These results indicate that the fabric-based electrodes possess attractive explosive sensing abilities, comparable to those of conventional screen-printed voltammetric electrodes.

The repeatability of the GORE-TEX fabric-based explosive sensor was subsequently examined. The investigation consisted of casting 60 µL of 20 µg/mL DNT or TNT solutions onto the GORE-TEX fabric-based sensor, recording the sensor’s response, and then replacing the test sample with phosphate buffer and measuring its response in the same manner. This cycle was then repeated an additional nine iterations and the sensor response was recorded in each experiment for a scanned potential of −0.6 to 1.2 V (A) and −0.5 to 1.1 V (B) for DNT and

Fig. 4. (A) Effects of repetitive bending on the cyclic voltammograms of the GORE-TEX fabric-based sensor in 10 mM potassium ferrocyanide. Ten bending operations were conducted between either two consecutive cyclic voltammetric measurements. Bending time, 1 s; release time, 1 s. Bending was applied at an inward angle of 180° with a 1 mm bending radius. Scan rate: 100 mV s$^{-1}$. (B) Current profiles recorded from the redox current of ferrocyanide after 10 such bending operations.

Fig. 5. Square wave voltammograms (left) of GORE-TEX fabric-based sensors towards the sensing of DNT (A) and TNT (B) in 0–50 µg/mL. (i–vi) and corresponding calibration plots (right). Potential step, 4 mV; Amplitude, 25 mV; Frequency, 20 Hz. Current in calibration plots are sampled at −0.86 V (A) and −0.75 V (B).
TNT, respectively. The SWV results are shown in Figure 6. This fabric-based sensor demonstrated a well-defined response towards the detection of DNT and TNT, showing minimal decay in the 10th evaluation of DNT ($RSD = 8.5\%$ for DNT and $2.6\%$ for TNT). These results indicate the potential of the GORE-TEX fabric-based sensor to detect explosives in a repetitive fashion. The fabric-based sensor must be able to yield operation over extended periods with minimal deterioration of the sensor performance even under multiple sampling operations.

Laundry washing represents another routine activity that may affect the performance of textile-based sensors. Here, chemical deterioration (originating from the detergent) rather than mechanical deterioration may affect the electrochemical behavior. Figure 7 illustrates the influence of washing of the GORE-TEX fabric-based electrodes upon their voltammetric response for $20 \mu g/mL$ TNT. The GORE-TEX fabric-based sensors were subjected to a traditional laundry cycle in a typical household washing machine using commercially available Tide® liquid detergent along with additional clothes. As can be seen in Figure 7 (ii and iii), the GORE-TEX fabric-based sensor showed similar voltammetric response even after repeated washing. A slight shift in the reduction peak potential was observed after the first washing; however, further washing did not have any effect on the peak potential. It should be noted that the majority of the GORE-TEX fabric-based sensors did not degrade significantly after one laundry routine. However, after three laundry cycles, only half of the original 10 GORE-TEX fabric-based sensors remained functional and maintained their sensing properties. Common causes of laundry-induced degradation include splitting of the fabric, cracking/breaking of the carbon layer, and disconnection of the conductor traces.

Detection of explosive vapors is expected to meet the growing demands for remote security sensing. Preliminary experiments demonstrated the ability of the GORE-TEX fabric-based sensor, modified with a hydrogel electrolyte, for the detection of DNT vapor. DNT powder was stored in a sealed glass jar for 30 min to mimic a hypothetical situation where an explosive agent is concealed and transported within baggage. Figure 8 shows the voltammetric detection of DNT vapors using the GORE-TEX fabric-based sensor at increasing exposure durations using SWV. A characteristic reduction peak is observed (at $-0.63$ V vs. Ag/AgCl). As expected, the response to the DNT vapor increases upon increasing the exposure time from 0 to 60 min.
4 Conclusions

We have examined the influence of various textile substrates upon the detection properties of thick-film electrochemical sensors. Cotton, polyester, and GORE-TEX fabrics were compared in order to determine a suitable textile electrode substrate that would facilitate the direct printing of an electrochemical sensor onto various fabrics using conventional screen-printing methods. The superior water-proof properties of the GORE-TEX fabric were shown to be particularly attractive for fabricating and operating such printable textile-based sensors. The GORE-TEX fabric was determined to be an excellent substrate material for supporting screen-printed electrodes and was characterized by its high degree of hydrophobicity, minimal sample absorption, excellent printing quality, and preservation of electrochemical activity against repeated bending operations. The electrochemical sensing properties of such GORE-TEX based printed electrodes were examined and their ability to detect nitroaromatic explosives was demonstrated. Further assessment of the durability and reliability of the GORE-TEX substrate for extended periods of use will lead to the development of field-deployable security and soldier monitoring systems integrated onto conventional garments. The results indicate the potential of textile-based screen-printed sensors for future security and military applications. With further development, the same sensing paradigm can be applied towards the detection of other explosives, particularly widely-used homemade explosives today. Current efforts are aimed at expanding the textile-based detection towards additional chemical agents of security relevance. Such activity will enhance the protection of soldiers and first responders in hazardous situations. These future applications would benefit from the integration of the necessary supporting electronic control, real-time information display, and alert functionality to enable field-based utility and to realize true ‘lab-on-a-textile’ functionality.

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