DOI: 10.1002/elan.201400537

Tattoo-Based Wearable Electrochemical Devices: A Review

Amay J. Bandodkar,[a] Wenzhao Jia,[a] and Joseph Wang*[a]

Abstract: This article provides an overview of the recent advances in the field of skin-worn tattoo-based wearable electrochemical devices, including electrolyte and metabolite sensors, biofuel cells and batteries. Temporary tattoos are attractive platforms for fabricating skin-worn devices. Body-compliant wearable electrochemical devices on temporary tattoos couple highly favorable substrate-skin elasticity with an attractive electrochemical performance. For example, tattoo-based "skin-like" sensors can be used for real-time non-invasive analysis of key electrolytes and metabolites, leading to remarkable sensing capabilities. Continued progress has been made also towards developing skin-worn flexible energy harvesting and storage devices to power wearable health monitors and other devices. Key requirements and challenges that confront researchers in this exciting area of skin-worn electrochemical devices are discussed.

Keywords: Wearable sensors · Non-invasive monitoring · Printable flexible devices · Skin · Screen printing · Biofuel cells · Batteries · Electrochemical sensors

1 Introduction

1.1 Wearable Devices

Wearable sensors have received a major recent attention owing to their considerable promise for monitoring a wearer's health [1,2]. Medical interest for wearable systems arises from the need for monitoring patients over long periods of time. These devices have the potential to continuously collect vital health information from a person's body and provide this information to them or their healthcare provider in a timely fashion. Such on-body monitoring can alert the wearer of any imminent health hazard and hence facilitate rapid corrective clinical action (outside of the hospital environment). A common example is minimally-invasive glucose biosensors towards effective closed-loop glycaemic control [3]. These developments hold considerable promise for maintaining and improving the quality of life while reducing medical costs. This is particularly true for monitoring older adults or patients with chronic diseases in home settings, in general, and particularly in remote locations (with limited or no personal access to doctors). On-body monitoring of performance markers (coupled to smartphone platforms) has also received considerable recent attention in connection to variety of sports, fitness and military applications [4–6]. While most early efforts on wearable fitness and biomedical devices have been devoted to the continuous monitoring of vital signs (such as heart rate, respiration rate, skin temperature) from physical signals, wearable chemical sensors have received limited attention. The introduction of new non-invasive chemical sensors would thus fill current gaps in wearable sensor technology, as desired for mobile health monitoring and remote diagnostics. Efforts have also been directed towards developing body-worn energy harvesting and storage devices to power wearable health and fitness sensors.

The present article provides an overview of a range of skin-worn tattoo-based wearable electrochemical devices, including amperometric and potentiometric sensors (aimed at transducing the chemical information from the wearer epidermis), biofuel cells and batteries, along with related challenges and opportunities.

1.2 Electrochemical Wearable Devices

Owing to their inherent miniaturization and low-power requirements, simplicity, speed and low costs, electrochemical devices meet the requirements of on-body wearable systems. Sweat, saliva and tears are three biofluids that contain multiple physiologically relevant chemical constituents and can be easily obtained in a continuous fashion for non-invasive real-time monitoring of these analytes. For example, the level of electrolytes (pH, sodium, ammonium, calcium) and metabolites (glucose, lactate, urea) in sweat and the skin interstitial fluid can provide valuable health information [7–11]. Similarly, salivary pH, lactate and electrolyte concentrations can be used to identify disposition towards developing dental caries [12], physical stress [13] and amount of salt intake [14], respectively. The levels of glucose [15], lactate [16], or neurotransmitters [17] in tears also hold vital health significance. Taking advantage of these correlations, several re-

[a] A. J. Bandodkar,[#] W. Jia,[#] J. Wang
Department of Nanoengineering, University of California San Diego
La Jolla, CA 92093, USA
*e-mail: josephwang@ucsd.edu

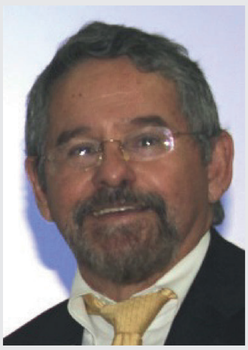
[#] These authors contributed equally to this work.

search groups have recently developed wearable electrochemical devices that can measure these and other analytes in a completely non-invasive user-friendly manner [18]. For example, early studies utilized partially-removable denture platforms for developing potentiometric sensors to monitor fluoride [19] and pH [20] levels of saliva. Recently, a tattoo-based resistive sensor for real-time detection of bacterial infection on tooth was demonstrated [21]. Similarly, we described a mouthguard-based sensor for continuous saliva lactate monitoring [13]. Researchers focused in the tears-based sensing domain have developed non-invasive flexible strip-based sensors for monitoring glucose levels in tears [17,22]. Recently, a wireless contact lens-based glucose [23] and lactate [16] sensors have also been reported. On the other hand, Diamond's group has carried out extensive work on developing monitoring sweat pH [24], sodium [8] and lactate [11] levels using textile [24], plastic [11] based patches. Gonzalo-Ruiz et al. fabricated a textile-based sensor patch for detecting chloride ions in human sweat [9]. Guinovart et al. developed cotton yarn based pH, NH_4^+ and K^+ sensors for wearable applications [25]. Similarly, our group demonstrated the ability of screen printing sensors directly on textiles for non-invasive physiological monitoring [26]. Researchers have also made efforts to develop flexible oxygen [27] and humidity [28] sensors. Though there have been several demonstrations of wearable devices for non-invasive monitoring, these sensors have a few limitations. Intimate contact between the sensor surface and sweat is critical for efficient functioning of a wearable sensor. Satisfying this condition is challenging in case of fabric-based sensors as conformal contact with the skin is restricted to limited regions. Furthermore, only limited types of fabrics are well suited for incorporating chemical sensors [29]. Plastic-based patch sensors usually are thick and have limited stretchability and hence don't conform well to human skin. Rub-on temporary tattoos are highly ergonomic and are always in intimate contact with the human skin and thus offer a unique platform for incorporating wearable sensors.

Amay J. Bandodkar is a doctoral candidate in the Department of NanoEngineering at UCSD. His research interests lie in the development of wearable electrochemical devices. He completed his undergraduate course from the Indian Institute of Technology-Banaras Hindu University (India) with the focus on biosensors and has been involved in several academic and industrial projects in India and Germany.

Wenzhao Jia is a postdoctoral scholar in the Department of NanoEngineering at the University of California San Diego. She is working on the development of wearable biosensors and biofuel cells. She received her Ph.D. in Chemical Engineering from the University of Connecticut. Her graduate research focused on the preparation of nanostructured functional materials for sensing and energy applications.

Joseph Wang is a SAIC Endowed Professor Distinguished Professor Director of the Center of Wearable Sensors, and Chair of Nanoengineering at the University of California San Diego. His current research focuses on synthetic nanomotors and nanomachines, wearable electrochemical devices, and nanobioelectronics.



2 Tattoo-Based Electrochemical Devices

2.1 Significance and Fabrication Protocol

The skin acts as the protective barrier between the internal body systems and the surrounding environment and provides primarily a sense of touch. Developing epidermal wearable devices requires different design and fabrication principles due to the unique mechanophysiology of our skin. Researchers have thus recently focused on developing skin-worn electronic devices that are in intimate contact with the wearer's body and mimic the properties of skin. Most recent attention has been given to lithographic-based skin-mounted flexible electronics developed by the groups of Rogers, Javey and Bao [30–32]. Diverse electronic devices capable of being bendable and stretchable have thus been reported. Such flexible lithographic devices have been used for real-time non-invasive monitoring of physical health and fitness parameters.

The realization of epidermal chemical sensing requires direct and continuous contact between the wearable electrochemical diagnostic device and the skin. Textile-based devices satisfy this requirement only partially, since the regions on the body where they are in intimate contact with the skin continuously are limited [33,34]. Use of textiles also limits the use of such devices to measure analyte concentrations only at these specific locations. Additionally, textile-based electrochemical devices can usually be incorporated on limited types of fabrics to obtain best results [29] and thus limits a wearer's freedom. Textile based sensors are expected to perform for long duration and thus sensor stability is a major challenge. In case of permanent textile sensors, the effect of washing on such devices is another major challenge that can potentially compromise the sensor stability when biorecognition molecules are involved. To address some of these concerns, researchers have ventured into developing flexible plas-

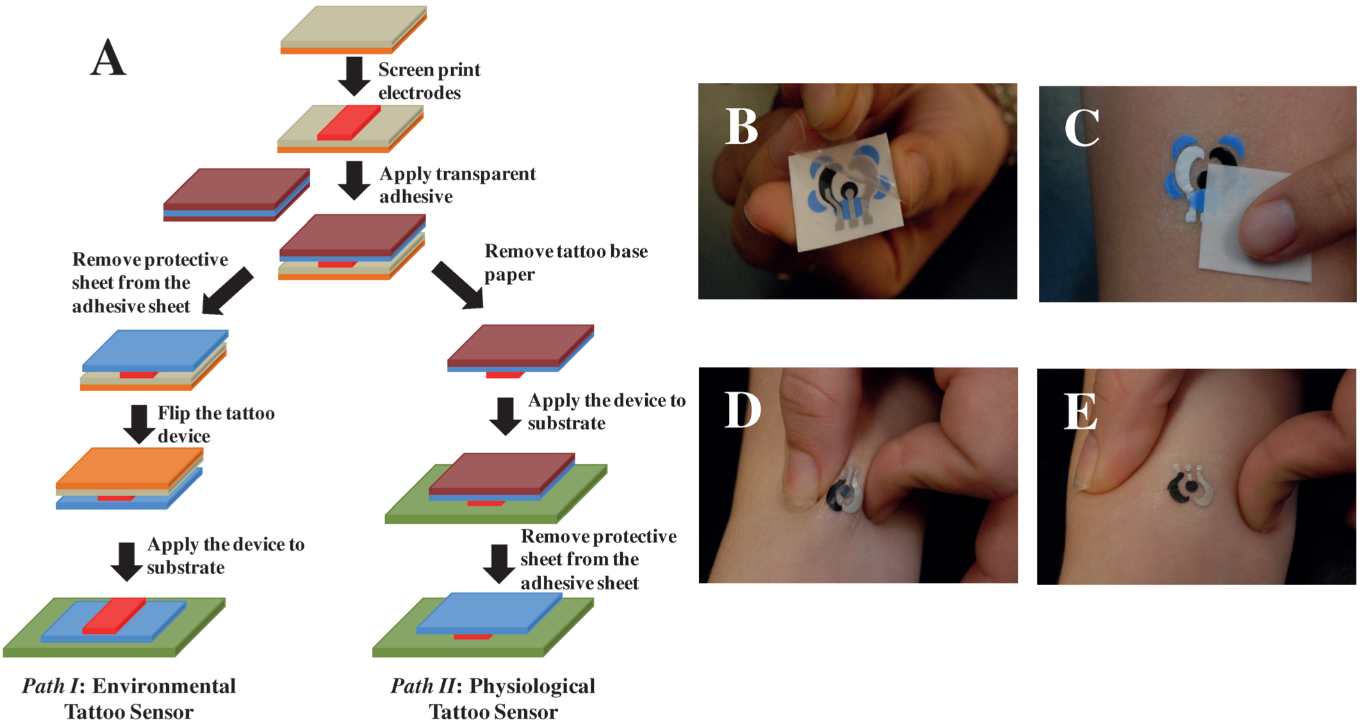


Fig. 1. Fabricating of printable tattoo-based electrochemical devices (A) Typical steps involved in fabricating screen printed tattoo-based sensing devices for environmental (path I) and physiological (path II) analyte monitoring. Photographs showing standard steps of (B) removing the transparent protective sheet and (C) gently sliding the tattoo base paper after dabbing it with water to apply a tattoo device to human skin. Images showing extent of mechanical stress experienced by a tattoo applied to a human subject during (D) stretching and (E) twisting of the underlying skin. From [35].

tic-based electrochemical patches [11]. Such skin adhesive patches can be easily applied to any location on the wearer's skin and since these are usually one-time use devices the issue of washing degradation is not a concern. However, such diagnostic tools have restricted body-compliance as these can only bend but cannot withstand stretching stress.

Our activity, reviewed in this article, has led to new methods for "printing" electrochemical devices directly onto temporary tattoo so people can wear them while performing their normal daily activities. The tattoo platform offers a unique opportunity to develop body-compliant electrochemical sensors that are continuously in contact with the human skin. The human epidermis experiences continuous complex bending and stretching stress while the body performs various routine activities. The extent of such deformations increases dramatically under extreme physical activities usually undertaken by athletes. Thus, the mismatch between the mechanical properties of the flexible devices and the human skin can lead to degraded performance and makes the wearer feel a bit uncomfortable. An ideal wearable device must combine its attractive electrochemical performance with resistance to mechanical stress under repeated bending and flexing while causing minimal intrusion in the wearer's daily routine.

Researchers must therefore consider developing wearable devices that have similar mechanical properties to that of the skin and thus act as a "*secondary skin*". Temporary tattoos have been used for decades as body art and are quite widely accepted by the masses. Such tattoos are inexpensive and attach firmly to the human skin even under severe mechanical deformations while the wearer hardly notices their presence on their body. Temporary tattoos thus represent extremely attractive platforms for fabricating body-compliant wearable electrochemical devices capable of extracting rich chemical information from our epidermis and transmit these analytical data wirelessly to a smartphone.

Leveraging on our expertise in screen printing technology we reported the first example of temporary tattoo-based electrochemical sensors [35]. This early study described the fabrication process involved in making such epidermal devices for both physiological and environmental monitoring. As illustrated in Figure 1A, this process involved the screen printing of active ink materials, like carbon and Ag/AgCl, on commercial temporary tattoo papers to form sensor electrodes with a variety of designs. Passive insulating ink printing is also carried out to seal interconnects, define electrode areas and also to enhance the aesthetics of the tattoo devices. Such design of synthetic epidermal sensors also opens up new opportunities for artistic explorations. Finely chopped carbon fibers are dispersed within the Ag/AgCl and carbon inks prior to initiating the printing process. Carbon fibers have a dual purpose: (1) by acting as reinforcement fillers they enhance the mechanical resiliency of the devices; (2) they behave as a conductive backbone and increase the conductivity of the printed electrodes. The printed electrodes can be modified with recognition elements and other reagents to obtain high-fidelity wearable electrochemical devices. The as-prepared tattoo devices can now be easily applied to a wearer's skin in a manner similar to any commercial temporary tattoos, i.e. the wearer first removes the transparent protective sheet from the tattoo device to expose the transparent adhesive and sticks it to the skin. Thereafter, the tattoo paper is moistened with water to dissolve the water soluble release agent and finally slide the paper to obtain the device firmly attached to the skin. The tattoo device can be coupled with a transceiver for wireless data transmission from the tattoo to any smartphone/laptop in a continuous fashion. A similar fabrication and on-body transfer process can be employed for tattoo-based epidermal biofuel cells and batteries. The following sections delineate the fabrication and performance of recently developed tattoo-based printable electrochemical devices, ranging from biosensors to batteries, capable of conformally adhering to the skin. The final section will deal with the challenges and plausible methods to address these as well as the immense growth potential of tattoo-based electrochemical devices.

2.2 Tattoo-Based Potentiometric Sensors

The human sweat contains a number of ions [36]. The concentration of several of these ions offers vital information about an individual's health [37] as well as his environment [38]. For example, monitoring of sodium levels in sweat reveals the extent of electrolyte imbalance [39] and has been used to detect Cystic Fibrosis [40]. Similarly, calcium concentrations in sweat have been used as an indicator of bone mineral loss for athletes during extensive physical activities [41] as well as in osteoporotic patients [37]. The pH of human sweat is an excellent parameter to monitor overall skin health conditions and dehydration [42]. Research has also pointed out that ammonia levels in human sweat can be considered as indicator of physical stress and hygiene conditions [43]. Sweat has also been an outstanding milieu for monitoring heavy metals present in the human body. Such monitoring is crucial for studying bioaccumulation of toxic trace metals entering an individual's body through the food chain or the respiratory path [44].

The diagnostic tools developed to date detect specific ions either optically [45] or electrochemically [18]. The latter gives a more accurate electrolytic concentration and thus is a preferred technique for applications requiring high precision. Such electrochemical measurements rely on ion-selective potentiometric sensors [46–50]. Classical potentiometric sensors consist of liquid-junction based indicator and reference electrodes. The liquid-junction is important for obtaining a stable and reproducible potential at both reference and indicator electrodes. However, liquid-junction based potentiometric sensors are not preferred for wearable applications as leakage of the solution will be deleterious to the electrode performance and also cause nuisance to the wearer. The classical potentiometric sensors are also constructed using rigid materials (e.g., glass, polymers, etc) that do not comply with the elastic nature of the human skin, making such potentiometric sensors uncomfortable to the wear.

The tattoo ion-selective electrodes were thus cautiously designed to circumvent the above mentioned major limitations faced by the classical potentiometric sensors. Considerable work has been done on developing all-solid-state indicator electrodes [51,52]. A similar methodology was considered while fabricating the indicator electrodes of the tattoo-based sensors. As compared to indicator electrodes, few efforts have been devoted towards developing an all-solid-state reference electrode. Though some groups have demonstrated all-solid-state reference electrodes, most of these still require incubation of the electrode in standard solutions when not in use [53]. Such a step is incompatible with the tattoo platform. Efforts were thus made to identify a suitable technique to develop an all-solid-state reference electrode that provides a stable reference potential without the need for special storage conditions. Initially, we relied on all-printed reference electrode fabricated by screen printing an additional layer of KCl-saturated insulator layer on the printed Ag/AgCl electrode [54]. Thereafter, a more reliable technique of coating the printed Ag/AgCl electrode with NaCl saturated polyvinyl-butyral (PVB) polymer was adopted [55–57]. The printable-electrode tattoo platform offers a unique opportunity to develop body-compliant potentiometric sensors for monitoring transient electrolyte concentration profiles and alert the wearer of any imminent health risks. As discussed later, the tattoo-based potentiometric sensors withstand significant mechanical stress with minimal effect on their response. Figure 2 shows the various tattoo-based potentiometric sensors demonstrated to date. The next sub-sections provide the reader with a detailed discussion about the fabrication and performance of these electrolyte-specific tattoo sensing devices.

2.2.1 Tattoo-Based pH Sensor

Screen printing technology offers great leeway for designing high-performance wearable sensors of different artistic designs. Taking advantage of this property, the pH tattoo sensor was given an aesthetically looking "Smiley Face" design [54]. The two eyes of the "Smiley face" were printed using carbon and Ag/AgCl inks and acted as the indicator and reference electrodes, respectively. The contact pads for the electronic readout were realized in the form of the two ears. The top-most blue color insulator layer defined the entire face and also isolated the underlying Ag/AgCl inter-connects between the electrodes (eyes) and contact pads (ears). The printed bare carbon and Ag/AgCl electrodes cannot be used directly for selective pH measurements. Hence, the two electrodes were

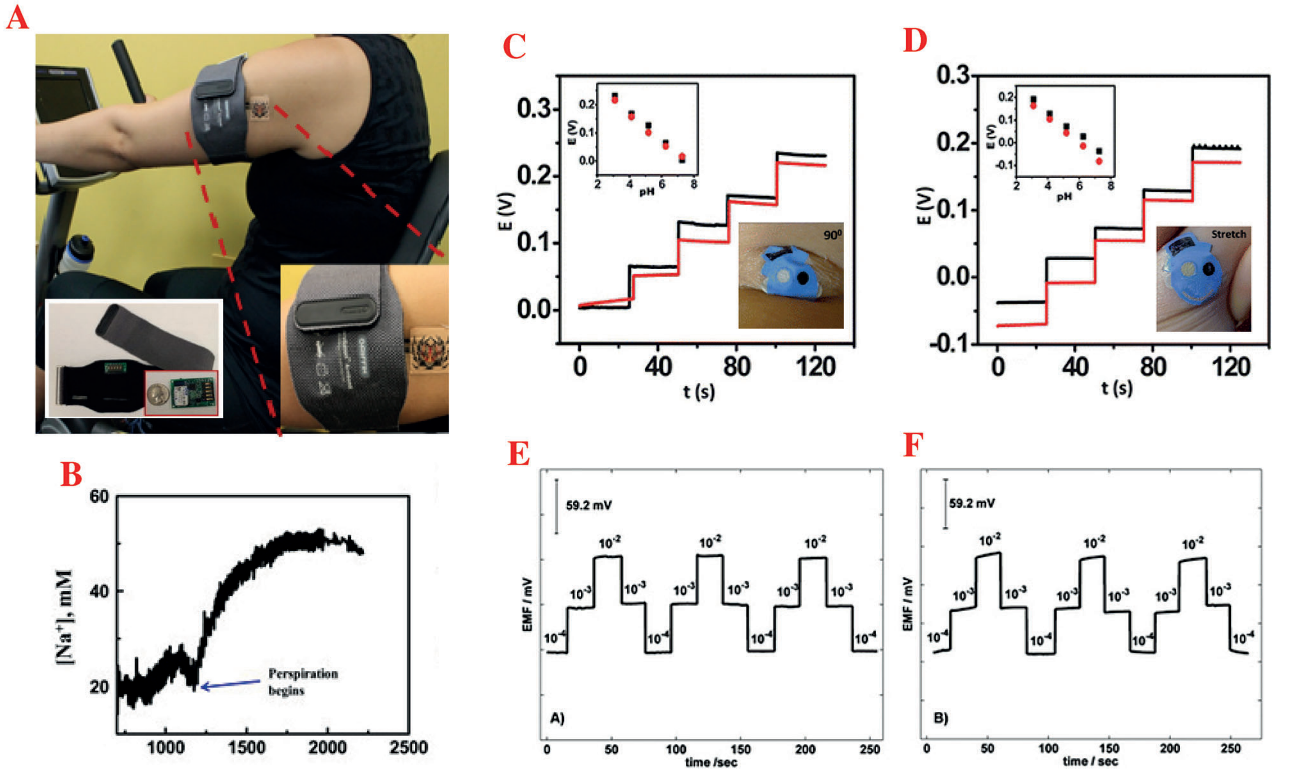


Fig. 2. Potentiometric tattoo sensors: (A) A subject wearing a sodium tattoo sensor (right bottom inset) along with the wearable wireless transceiver (left bottom inset). (B) Real-time sodium concentration profile in a subject's sweat monitored by the sodium sensor. (C) Response of the pH tattoo sensor to repeated bending stress (inset shows the tattoo when bent by 90°). (D) Response of the pH tattoo sensor to repeated stretching stress (inset shows the tattoo during stretching). (E) Typical response of an ammonium tattoo sensor to varying ammonium levels in water. (F) Hysteresis study performed using an ammonium tattoo sensor when placed over cellulose filter paper saturated with solutions of different ammonium concentrations. From [54–56].

further modified for obtaining specificity. Biocompatibity is an eminent condition that each component of a wearable device must comply with. Polyaniline has been widely used for tissue engineering [58] and in-vivo diagnostics [59]. Moreover, the conductivity of polyaniline has been reported to have excellent correlation with proton concentration and thus it has been widely used for fabricating pH sensors [60]. From fabrication view point, polyaniline with controlled thickness and morphology can be easily obtained on electrode surfaces by an electrochemical polymerization technique [61]. Polyaniline was thus selected as a pH-responsive component while fabricating the pH tattoo sensor. On the other hand the bare Ag/AgCl electrode was stabilized by printing a KCl-saturated insulator layer. The high concentration of the chloride ion within the insulator layer provided a stable reference electrode irrespective of the analyte composition.

Characterization of the sensor in the physiologically relevant pH range of 3–7 revealed a sub-Nernstian response (50.1 mV/pH). The pH of the human perspiration changes with time and depends on several factors like hydration level, physical activity intensity among others [42] and thus the pH tattoo must be able to measure such transient variations. The capability of the pH tattoo sensor to perform such dynamic study was examined using a hysteresis study which revealed that the tattoo responds almost instantaneously to changing pH solutions with minimal memory. This study proved that the pH tattoo sensor can measure dynamic pH changes rapidly without memory effect. The device was also subjected to repeated bending (180°) and stretching (10%) fatigue cycles and the response was measured after regular intervals (Figure 2C,D). These mechanical studies revealed minimal effect of such strains on the tattoo response. Ultimately, three pH tattoos were applied to the neck, forearm and lower back of a human subject for real-time measurements of his sweat pH. The response recorded by the pH tattoo correlated well with the pH values logged by a commercial pH meter. The study thus underscores the promise of the pH tattoo for accurate monitoring sweat pH in a completely user-friendly manner.

2.2.2 Tattoo-Based Sodium Sensor

The immense importance of continuous monitoring of sodium levels in the sweat urged us to develop a tattoo-based sodium sensor that can inform the wearer about their electrolyte imbalance in a non-invasive manner [8]. Poly-vinylchloride membrane based potentiometric sensors have been developed for in-vivo applications [62,63] and hence a similar technique was utilized for developing tattoo-based sodium sensors. The all-solid-state sodium sensor was fabricated by casting a poly-vinylchloride membrane containing a highly selective sodium ionophore (Selectophore grade sodium ionophore X) [55]. A stable reference electrode was obtained by a new technique consisting of coating the bare Ag/AgCl electrode with a layer of NaCl-saturated PVB membrane. The most attractive aspect of the new sodium-selective device has been the customized wearable Bluetooth transceiver that collects and wirelessly transmits real-time information from the tattoo sensor to any smartphone/laptop. Briefly, the transceiver consisted of an electrochemical analyzer-on-a-chip, an 8-bit low-power microcontroller (MCU, running custom scripts to perform the electrochemical measurements), a Bluetooth v2.1+EDR 2.4 GHz wireless module, voltage regulator, USB battery charger IC, and all associated passive components mounted on a 30 mm × 45 mm printed circuit board (PCB) and was powered by a rechargeable Li-ion 2032 button-cell battery (recharged via a micro-USB connector used for flashing the MCU). Data was relayed at 1 s intervals to a Bluetooth-enabled PC via a serial data stream. A spring-loaded pressure connector was leveraged in order to interface with the Na-tattoo epidermal sensor. The tattoo sensor consisted of flexible PET-based rectangular connectors that can reduce noise level and easily interface with the spring-loaded connector of the transceiver for data recording [55]. The interface can be made more robust by including an edge connector for more efficient interface with the PET connectors of a tattoo device. A hybrid fabrication protocol was adopted which combined laser and screen printing to obtain sensors that could have any design that a wearer desires. Continuous flow of fresh sweat towards the sensor surface is critical towards real-time sweat analysis. This was achieved by incorporating a fluidic channel consisting of a cellulose acetate sink and kapton film-based fluidic walls for directed flow of sweat. The tattoo sensor was characterized using NaCl solutions as well as artificial sweat. Memory, temperature and aging effects were examined. Special attention was given to study the effect of mechanical stress on the sensors by repeatedly bending, stretching and poking the sensor using a tensile test machine. The sodium sensor was bent by 180° for a total of 100 times while a successively increasing tensile strain applied to the tattoo sensor up to 26%. The study revealed that such strenuous conditions have negligible effect of the sensor response and hence they can be used in real-life scenarios. The tattoo sensor was applied to real-time monitoring of sodium in human subjects using the tattoo sensors coupled with the wireless transceiver (Figure 2A,B). The promising results obtained from the study highlight the applicability of the developed device in real-life scenarios. The concept could be extended for monitoring the electrolyte balance in sweat and particularly the sodium/potassium ratio using a dual-tattoo potentiometric sensor.

2.2.3 Tattoo-Based Ammonium Sensor

Ammonium level in the sweat indicates the extent of physical stress and is also relevant from the hygienic point of view. A tattoo-based potentiometric ammonium sensor for continuous ammonium concentrations in the sweat was thus developed [56]. The sensor was printed on the tattoo paper in the form of a “two-petal flower” shape. The Ag/AgCl petal performed as the reference electrode while the carbon stamen acted as the indicator ammonium electrode. The blue insulator-based sepals were added to the design to enhance the aesthetics of the sensor. The ammonium electrode was developed by casting a nonactin-based polyvinyl chloride membrane on the carbon stamen electrode, while the reference electrode was further coated with a NaCl saturated PVB membrane. Similar to the sodium tattoo sensor, a fluidic channel was incorporated within the device for directed flow of fresh sweat over the sensor surface. The tattoo response for varying ammonium levels was measured and the tattoo responded in a near-Nernstian response with minimal hysteresis (Figure 2E,F**)**. Repeated mechanical deformations of the sensor too had negligible effect on its response. Several human subjects were recruited to test the tattoo sensor in real-life scenarios. The study revealed that the tattoo could measure the ammonium levels in perspiring human subjects and thus can be used for daily tracking of ammonium in sweat.

2.3 Tattoo-Based Amperometric Sensors

Tattoo devices have been demonstrated for electrolytic detection based on potentiometry, while they are able to sense metabolites and other electroactive hazards present in surroundings of the wearers by voltammetry [35]. Square wave voltammetry was applied for the detection of 2,4,6-trinitrotoluene by a tattoo device. The sensing of uric acid and ascorbic acid was in connection with cyclic voltammetry [35]. The detection of other metabolites can be established based on enzymatic catalysis, because of their high biocatalytic activity and specificity, which enables the selective detection of individual substance in a complex mixture, such as blood, sweat or urine [64]. The device contains a biological recognition element, enzymes that selectively catalyze analytes in sweat and produces an electrical signal that correlates with the analyte concentration.

Lactate, one of the most important biomarkers of tissue oxygenation, has been widely used by coaches, exercise physiologists, and sports physicians to monitor an athlete’s performance [65]. Lactate is produced when anaerobic process is invoked and increases its levels in blood [66]. To avoid traditional repetitive finger blood draws in rigorous training, we seeked to design an “NE” lactate tattoo biosensor (Figure 3A) to offer useful insights into the temporal dynamics of lactate concentration in the perspiration in a completely non-invasive manner [67]. The epidermal lactate biosensor was fabricated with

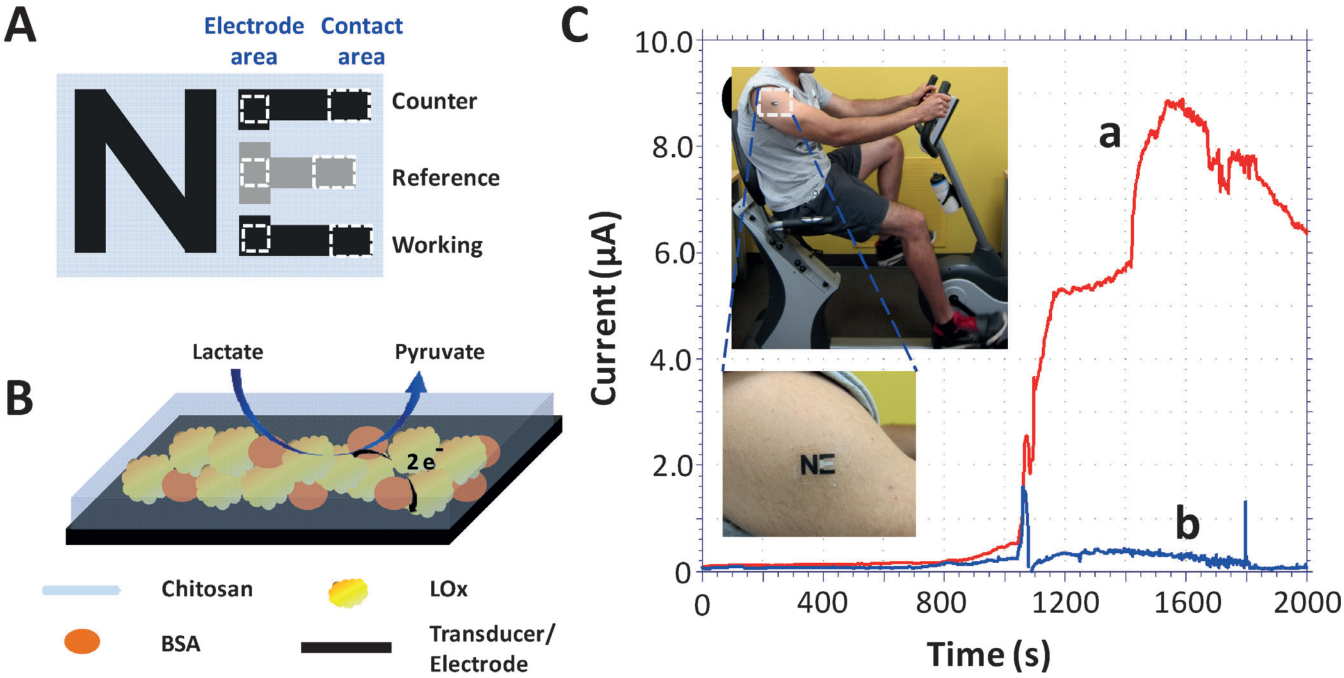


Fig. 3. A) Schematic illustration of a three-electrode "NE" tattoo biosensor for electrochemical epidermal monitoring of lactate. B) Constituents of the reagent layer of the working electrode which is coated by biocompatible polymer (chitosan). C) Response of the LOx- (a) and enzyme-free (b) tattoo biosensors during the exercise regimen. Inset, an "NE" lactate biosensor applied to a male volunteer's deltoid. From [67].

carbon-nanotube/tetrathiafulvalene mediated lactate oxidase as the recognition layer, covered by a biocompatible chitosan overlayer that functioned as a physical barrier and limited the efflux of the catalytic backbone from the tattoo onto the underlying epidermis.(Figure 3B) The lactate tattoo biosensor was operated at a very low potential of +0.05 V (vs pseudo Ag/AgCl) for the chronoamperometric detection of lactate, and has a linear range up to 20 mM. The sensors exhibited high operational stability during prolonged periods of operation, and less than 10% decay for a long term storage of up to 5 months. The mechanical deformations of bending/stretching stains had negligible effects on the tattoo sensor response. Since the detection is at a potential of 0.05 V, interferences can be excluded. The responses of ascorbic acid, uric acid, glucose and creatinine were negligible compared to that of lactate. The specificity of the tattoo biosensors were further validated when applied during on-body tests. The lactate biosensor was applied to the skin of human subjects, and the corresponding sweat lactate temporal profiles were recorded (Figure 3C). Simultaneous assessment using control epidermal tattoo sensors without LOx enzyme confirmed the high specificity towards sweat lactate. The temporal lactate profiles demonstrated that the new wearable lactate biosensor platform performs desirably under fitness routines, thereby substantiating its utility for the noninvasive assessment of lactate levels and degree of physical exertion. Current efforts aim at further miniaturizing and integration of the electronic interface, data processing, and wireless transmission of the results.

3 Electrochemical Tattoo-Based Energy Devices

While extensive efforts have been devoted to the development of wearable health and fitness monitoring systems, limited efforts have focused on developing body-worn energy harvesting and storage devices to power the these sensing systems. Early efforts have resulted in the development of flexible batteries [68], piezoelectric nanogenerators [69], microsupercapacitors [70] and endocochlear-potential-based biobatteries [71]. In this section we describe recent activity aimed at designing tattoo-based energy harvesting and storage biofuel-cell and battery devices with favorable mechanical properties. Such integration of flexible energy harvesting and storage devices onto the skin will bring new opportunities beyond what can be achieved by their current rigid counterparts and will facilitate the creation of fully autonomous systems.

3.1 Epidermal Tattoo Biofuel Cells

In this section we describe the development of non-invasive biofuel cells (BFC) than can harvest energy from lactate present on the epidermis. As a promising alternative source of sustainable electrical energy, biofuel cells are devices that convert chemical energy into electricity through biocatalytic reactions [72–74]. BFCs designed for harvesting energy from animals are commonly based on glucose as the fuel, along with oxygen [75,76], since these compounds are present in many living organisms. These implantable devices have been previously designed for harvesting energy from fruits [77], insects [78] and other

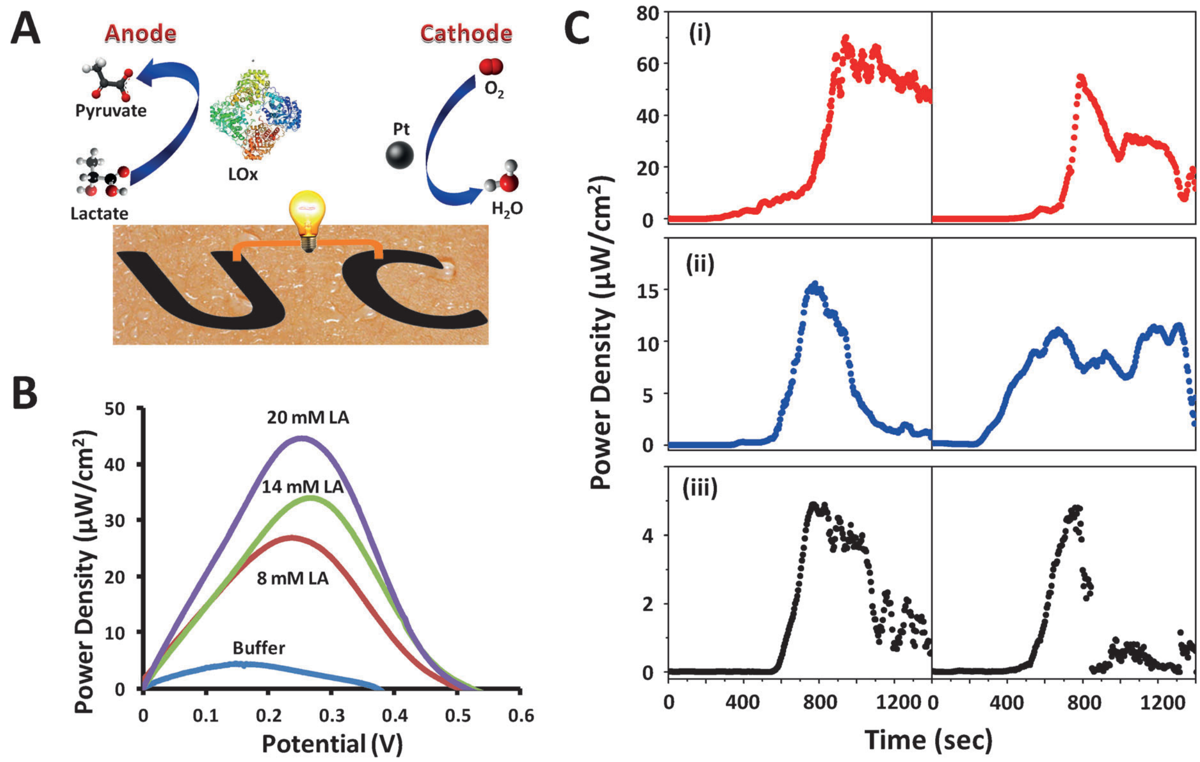


Fig. 4. A) Illustration of the epidermal tattoo BFC. B) Power density of the tattoo BFC at varying lactate (LA) concentrations in 0.2 M McIlvaine buffer solution (pH 5.5). C) Real-time power-density profiles during cycling activity of 6 human subjects: I) low fitness level, II) intermediate fitness level, III) high fitness level. From [82].

small animals [79–81]. Unlike implanted BFCs that must meet the stringent criteria of biocompatibility, sterilization and long operational stability, non-invasive BFCs that can use chemical fuels present on the epidermis represent an attractive strategy. Moreover, epidermal BFCs are less limited by oxygen than implanted BFCs.

In order to scavenge substantial amount of power from wearer epidermis, lactate was selected as the fuel of the tattoo BFC due to its high concentration present in human sweat. The epidermal tattoo BFC was built based on the oxidation of sweat lactate and the reduction of oxygen for the anodic and cathodic compartments, respectively (Figure 4A) [82]. Similar as abovementioned lactate tattoo sensors, the configuration of bioanode was made from CNT/TTF mediated LOx and efficient lactate oxidation was achieved. For a 14 mM lactate solution, the oxidation current of the bioanode can reach 0.2 mA/cm^2 at potential of 0.1 V. Commercial platinum black has been demonstrated as a good catalyst for oxygen reduction at suitable potential for the applications in (bio)fuel cells. The cathode for the UC BFC was coated with Pt black and a Nafion layer. This configuration of the BFC was able to generate 25, 34 and 44 μW/cm^2 for 8, 14 and 20 mM lactate, respectively, during in vitro experiments (Figure 4B). The tattoo BFC can stand repeated mechanical deformation and there was minimal loss in power density (less than 15%) after 50 bending/stretching iterations. The tattoo BFC was tested with artificial sweat containing 14 mM lactate and the results showed that it was stable during first two weeks, with less than 10% decrease in the power density; it maintained over 50% of the original value after one month storage.

When consented subjects wore the tattoo BFCs, substantial power was obtained directly from the wearers. More interestingly, the maximum power densities fall into three ranges depending on the fitness level of the wearers. (Figure 4C) For volunteers who are less active (< 1 physical activity per week), the maximum of the power density can reach up to 70 μW/cm^2; for the intermediate-fitness-level group (between 1 and 3 bouts of physical activity per week), the obtained maximum power density was in the range of 10–20 μW/cm^2; for the most active subjects, the power densities were typically less than 5 μW/cm^2. Hence, the maximum value greatly depends on the lactate concentration in the sweat; the more active the person, the lower concentration of lactate. Additionally, the tattoo BFC showed proved wearing stability with similar power outputs for repeated activity over 8 h. Current efforts aim at improving the power generation of the tattoo BFC, integration of the energy storage device and realization of powering wearable electronics.

3.2 Skin-Worn Tattoo-based Alkaline Batteries

Conventional batteries provide high power and are preferred for critical large scale applications. Since the open circuit potential and current density are sufficient to directly power electronics, it is very promising to fabricate

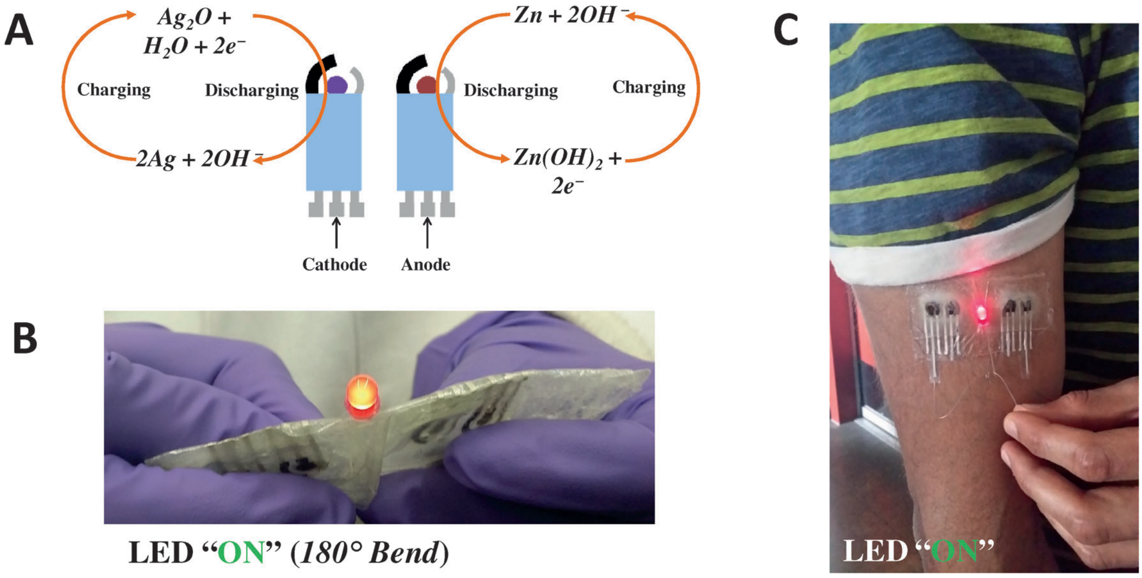


Fig. 5. Skin-worn printable-tattoo batteries. A) Typical redox reactions at the negative and positive electrodes. B) Demonstration of the performance of the tattoo battery under deformed conditions. C) Demonstration of practical utility of the tattoo battery for lighting a red LED after transfer onto skin. From [84].

portable, wearable, thin-film batteries as power supply [83]. Recently, our group has developed a tattoo-based Ag-Zn alkaline battery (Figure 5A) [84]. Zinc-based batteries provide an attractive alternative to Li-ion batteries because of the extensive global reserves of zinc. In addition, Ag–Zn cells are safer and have lower toxicity as they make use of the water-based electrolytes, compared with Li-ion batteries which rely on hazardous nonaqueous solvents. The Ag-Zn cells can be fabricated without a glove-box; the possibility to develop all-printed batteries makes it a better choice for wearable applications.

Key components of the tattoo battery (electrode materials, electrolytes and separator) were carefully selected for robustness and endurance of the battery. The new flexible battery was fabricated by screen printing carbon electrode onto the tattoo paper. Ag and Zn were electrodeposited on the active carbon electrode by chronopotentiometry. Polyacrylic acid (PAA) gels containing LiOH and ZnO were used for the electrolytes for the anode and cathode compartments, and the former one was also used for ionic contact between the two compartments. A PDMS film was employed to seal the battery. The tattoo battery was characterized by charging-discharging at the rate of 1.4 $mA\,cm^{-2}$ for 12 cycles (has a discharge capacity of 2.1 $mA\,h\,cm^{-2}$ for 13 cycles) maintaining an efficiency of 72%. The effect of mechanical deformations on the performance of the tattoo battery was further studied. The results demonstrated that the tattoo batteries can undergo repeated bending by 180° with a 34% decrease in the galvanostatic discharge capacity after 100 bends, while with 11.1% stretching stain, the discharge capacity decreased significantly to 18% of the initial value. Figure 5B shows the tattoo battery bended 180° was still able to light up a LED. Most importantly, we demonstrated the epidermal application of the new tattoo battery in real-life scenarios (Figure 5C). A consent volunteer wore two tattoo batteries connected in series on his deltoid to power a red LED, which indicated that the tattoo battery meets the demands of wearable electronics, offering attractive flexibility and good discharge capacity to power wearable electronics.

4 Challenges and Opportunities

We have surveyed recent advances in body-compliant tattoo-based wearable electrochemical devices, including skin-worn potentiometric and amperometric sensors, biofuels and batteries. By combining well-established screen printing, advanced surface functionalization, modern potentiometric and amperometric methods, BFCs and alkaline battery technology with temporary tattoos we have been able to demonstrate a variety of wearable non-invasive tattoo-based electrochemical devices. Very recently we also demonstrated stripping voltammetry-based tattoo sensors for monitoring trace metals in human perspiration [85], and iontophoretic-amperometric hybrid tattoo sensor for non-invasive subdermal glucose monitoring [86]. Such body-compliant wearable devices combine an attractive performance of electrochemical devices with a favorable substrate-skin elasticity of temporary tattoos and resistance to mechanical stress. Our initial demonstrations have already established that the new conformable electrochemical devices have immense scope for real-world applications. Such development of skin-worn metabolic and electrolytic sensors complements the widespread use of wearable devices for monitoring of vital signs from physical signals. The new wearable sensing platforms can thus yield extremely useful insights into the health, fitness and performance status of individuals.

The above sections have illustrated that the capabilities of printable tattoo-based electrochemical devices have advanced very rapidly in recent years. The successful realization of skin-worn electrochemical sensors requires innovative approaches for addressing major challenges of calibration, fouling and related offsets and stability, and longer on-body durability under mechanical stress. Tattoo-based devices are expected to be worn for short durations as compared to their implantable counterparts and hence leaching of reagents is not a critical issue. Yet, efforts must be made to enhance the retention of the various reagents to the sensor surface to avoid any possible leaching. The current devices are highly flexible and can withstand an extreme bending stress without much deterioration. However, despite their favorable substrate-skin elasticity, these devices have limited stretchability. Efforts should thus be made to make them more stretchable in connection to new low-cost large-scale fabrication techniques. The effect of washing on the tattoo device performance must be thoroughly studied while developing epidermal tattoo sensors that are expected to perform for long durations. Leaching of reagents and need for re-calibration are some of the other challenges that researchers will face when developing long-lasting tattoo-based devices. Additionally, the tattoo-biosensing concept could be expanded towards the detection of additional biomarkers present in sweat (e.g., cytokines) toward the monitoring of human performance and health. Such expansion would require further innovations owing to the trace (nM-pM) levels of these markers in sweat and the requirement for regeneration of the free receptor. Using the skin-mounted tattoo sensors for monitoring the surrounding environment during normal activity could further contribute to our security, health and wellness. Additional efforts should be devoted to the development of digital signal processing and algorithms and to the integration of a flexible electronic backbone, power source, and wireless-communication infrastructure. With continued innovation and detailed attention to key challenges, it is expected that skin-worn electrochemical sensors will play a major role in the emergent body sensor networks arena towards a plethora of diverse applications.

Acknowledgements

This work was supported by the *Nano-Bio Manufacturing Consortium* and *Samsung Inc*.

References

[1] L. Atzori, A. Iera, G. Morabito, *Comput. Netw.* **2010**, *54*, 2787–2805.
[2] A. J. Jara, M. A. Zamora, A. F. G. Skarmeta, *Personal and Ubiquitous Computing* **2011**, *15*, 431–440.
[3] J. Wang, *Chem. Rev.* **2008**, *108*, 814–825.
[4] L. Grajales, I. V. Nicolaescu, *International Workshop on Wearable and Implantable Body Sensor Networks, Proc.* **2006**, 154–157.
[5] S. Led, J. Fernandez, L. Serrano, *Proc. 26th Ann. Int. Conf. IEEE Engineering in Medicine and Biology Society*, Vols 1–7 **2004**, *26*, 3318–3321.
[6] C. T. Lin, L. W. Ko, M. H. Chang, J. R. Duann, J. Y. Chen, T. P. Su, T. P. Jung, *Gerontology* **2010**, *56*, 112–119.
[7] H. Minamitani, Y. Suzuki, A. Iijima, T. Nagao, *Ieice T Inf Syst* **2002**, *E85d*, 22–29.
[8] B. Schazmann, D. Morris, C. Slater, S. Beirne, C. Fay, R. Reuveny, N. Moyna, D. Diamond, *Anal. Meth.* **2010**, *2*, 342–348.
[9] J. Gonzalo-Ruiz, R. Mas, C. de Haro, E. Cabruja, R. Camero, M. A. Alonso-Lomillo, F. J. Munoz, *Biosens. Bioelectron.* **2009**, *24*, 1788–1791.
[10] A. Tura, A. Maran, G. Pacini, *Diabetes Res. Clin. Pract.* **2007**, *77*, 16–40.
[11] D. Khodagholy, V. F. Curto, K. J. Fraser, M. Gurfinkel, R. Byrne, D. Diamond, G. G. Malliaras, F. Benito-Lopez, R. M. Owens, *J. Mater. Chem.* **2012**, *22*, 4440–4443.
[12] A. J. Preston, W. M. Edgar, *J. Dent.* **2005**, *33*, 209–222.
[13] J. Kim, G. Valdes-Ramirez, A. J. Bandodkar, W. Jia, A. G. Martinez, J. Ramirez, P. Mercier, J. Wang, *Analyst* **2014**, *139*, 1632–1636.
[14] M. Emorine, P. Mielle, J. Maratray, C. Septier, T. Thomas-Danguin, C. Salles, *IEEE Sensors J.* **2012**, *12*, 3124–3130.
[15] S. Iguchi, H. Kudo, T. Saito, M. Ogawa, H. Saito, K. Otsuka, A. Funakubo, K. Mitsubayashi, *Biomed. Microdevices* **2007**, *9*, 603–609.
[16] N. Thomas, I. Lahdesmaki, B. A. Parviz, *Sensor. Actuators B, Chem.* **2012**, *162*, 128–134.
[17] A. Kagie, D. K. Bishop, J. Burdick, J. T. La Belle, R. Dymond, R. Felder, J. Wang, *Electroanalysis* **2008**, *20*, 1610–1614.
[18] A. J. Bandodkar, J. Wang, *Trends Biotechnol.* **2014**, *32*, 363–371.
[19] H. Graf, H. R. Muhlemann, *Arch. Oral Biol.* **1969**, *14*, 259–263.
[20] H. Graf, H. R. Muhlemann, *Helv Odontol Acta* **1966**, *10*, 94–101.
[21] M. S. Mannoor, H. Tao, J. D. Clayton, A. Sengupta, D. L. Kaplan, R. R. Naik, N. Verma, F. G. Omenetto, M. C. McAlpine, *Nat. Commun.* **2012**, *3*, 763.
[22] H. Kudo, T. Sawada, E. Kazawa, H. Yoshida, Y. Iwasaki, K. Mitsubayashi, *Biosens. Bioelectron.* **2006**, *22*, 558–562.
[23] H. Yao, Y. Liao, A. R. Lingley, A. Afanasiev, I. Lahdesmaki, B. P. Oti, B. A. Parviz, *J. Micromech. Microeng.* **2012**, *22*, 075007–075016.
[24] S. Coyle, D. Morris, K. T. Lau, D. Diamond, F. Di Francesco, N. Taccini, M. G. Trivella, D. Costanzo, P. Salvo, J. A. Porchet, J. Luprano, in *Proc. 3rd Int. Conf. Pervasive Computing Technologies for Healthcare. IEEE*, **2009**, 1–6.
[25] T. Guinovart, M. Parrilla, G. A. Crespo, F. X. Rius, F. J. Andrade, *Analyst* **2013**, *138*, 5208–5215.
[26] J. R. Windmiller, J. Wang, *Electroanalysis* **2013**, *25*, 29–46.
[27] K. Mitsubayashi, Y. Wakabayashi, D. Murotomi, T. Yamada, T. Kawase, S. Iwagaki, I. Karube, *Sensor. Actuators B, Chem.* **2003**, *95*, 373–377.
[28] E. Zampetti, S. Pantalei, A. Pecora, A. Valletta, L. Maiolo, A. Minotti, A. Macagnano, G. Fortunato, A. Bearzotti, *Sens. Actuators B* **2009**, *143*, 302–307.
[29] M. C. Chuang, J. R. Windmiller, P. Santhosh, G. V. Ramirez, M. Galik, T. Y. Chou, J. Wang, *Electroanalysis* **2010**, *22*, 2511–2518.
[30] D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I.

Kim, R. Chowdhury, M. Ying, L. Z. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. G. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, *333*, 838–843.
[31] C. Wang, D. Hwang, Z. Yu, K. Takei, J. Park, T. Chen, B. Ma, A. Javey, *Nature Mater.* **2013**, *12*, 899–904.
[32] M. L. Hammock, A. Chortos, B. C.-K. Tee, J. B.-H. Tok, Z. Bao, *Adv. Mater.* **2013**, *25*, 5997–6038.
[33] E. P. Scilingo, F. Lorussi, A. Mazzoldi, D. De Rossi, *IEEE Sensors J.* **2003**, *3*, 460–467.
[34] Y. L. Yang, M. C. Chuang, S. L. Lou, J. Wang, *Analyst* **2010**, *135*, 1230–1234.
[35] J. R. Windmiller, A. J. Bandodkar, G. Valdes-Ramirez, S. Parkhomovsky, A. G. Martinez, J. Wang, *Chem. Commun.* **2012**, *48*, 6794–6796.
[36] C. J. Harvey, R. F. LeBouf, A. B. Stefaniak, *Toxicol. in Vitro* **2010**, *24*, 1790–1796.
[37] R. P. Heaney, *J. Intern. Med.* **1992**, *231*, 169–180.
[38] K. Mitsubayashi, M. Suzuki, E. Tamiya, I. Karube, *Anal. Chim. Acta* **1994**, *289*, 27–34.
[39] M. F. Bergeron, *J. Sci. Med. Sport* **2003**, *6*, 19–27.
[40] R. C. Stern, *New Eng. J. Med.* **1997**, *336*, 487–491.
[41] R. C. Klesges, K. D. Ward, M. L. Shelton, W. B. Applegate, E. D. Cantler, G. M. Palmieri, K. Harmon, J. Davis, *J. Am. Med. Ass.* **1996**, *276*, 226–230.
[42] D. Morris, K.-T. Lau, D. Diamond, F. Di Francesco, N. Taccini, M. G. Trivella, D. Costanzo, P. Salvo, J.-A. Porchet, J. Luprano, in *Pervasive Computing Technologies for Healthcare, IEEE*, London, **2009**.
[43] F. Meyer, O. Laitano, O. Bar-Or, D. McDougall, G. J. F. Heigenhauser, *J. Med. Biol. Res.* **2007**, *40*, 885–885.
[44] D. C. Hohnadel, F. W. Sunderman, Jr., M. W. Nechay, M. D. McNeely, *Clin. Chem.* **1973**, *19*, 1288–1292.
[45] D. Morris, S. Coyle, Y. Z. Wu, K. T. Lau, G. Wallace, D. Diamond, *Sensor. Actuat. B, Chem.* **2009**, *139*, 231–236.
[46] U. Oesch, D. Ammann, W. Simon, *Clin. Chem.* **1986**, *32*, 1448–1459.
[47] E. Bakker, E. Pretsch, P. Buhlmann, *Anal. Chem.* **2000**, *72*, 1127–1133.
[48] E. Pungor, *Anal Sci* **1998**, *14*, 249–256.
[49] R. P. Buck, *Anal. Chem.* **1974**, *46*, R28–R51.
[50] J. D. Krusejarres, *Med. Prog. Technol.* **1988**, *13*, 107–130.
[51] J. Bobacka, T. Lindfors, M. Mccarrick, A. Ivaska, A. Lewenstam, *Anal. Chem.* **1995**, *67*, 3819–3823.
[52] J. Bobacka, *Anal. Chem.* **1999**, *71*, 4932–4937.
[53] A. Kisiel, A. Michalska, K. Maksymiuk, E. A. H. Hall, *Electroanalysis* **2008**, *20*, 318–323.
[54] A. J. Bandodkar, V. W. Hung, W. Jia, G. Valdes-Ramirez, J. R. Windmiller, A. G. Martinez, J. Ramirez, G. Chan, K. Kerman, J. Wang, *Analyst* **2013**, *138*, 123–128.
[55] A. J. Bandodkar, D. Molinnus, O. Mirza, T. Guinovart, J. R. Windmiller, G. Valdes-Ramirez, F. J. Andrade, M. J. Schoning, J. Wang, *Biosens. Bioelectron.* **2014**, *54*, 603–609.
[56] T. Guinovart, A. J. Bandodkar, J. R. Windmiller, F. J. Andrade, J. Wang, *Analyst* **2013**, *138*, 7031–7038.
[57] T. Guinovart, G. A. Crespo, F. X. Rius, F. J. Andrade, *Anal. Chim. Acta* **2014**, *821*, 72–80.
[58] M. Li, Y. Guo, Y. Wei, A. G. MacDiarmid, P. I. Lelkes, *Biomaterials* **2006**, *27*, 2705–2715.
[59] T. Lee, D. Bang, Y. Park, S. H. Kim, J. Choi, J. Park, D. Kim, E. Kim, J. S. Suh, Y. M. Huh, S. Haam, *Adv. Healthcare Mater.* **2014**, *3*, 1408–1414.
[60] M. Kaempgen, S. Roth, *J. Electroanal. Chem.* **2006**, *586*, 72–76.
[61] S. Cosnier, *Anal. Bio. Anal. Chem.* **2003**, *377*, 507–520.
[62] M. E. Collison, G. V. Aebli, J. Petty, M. E. Meyerhoff, *Anal. Chem.* **1989**, *61*, 2365–2372.
[63] E. Lindner, V. V. Cosofret, S. Ufer, T. A. Johnson, R. B. Ash, H. T. Nagle, M. R. Neuman, R. P. Buck, *Fresenius J. Anal. Chem.* **1993**, *346*, 584–588.
[64] N. J. Ronkainen, H. B. Halsall, W. R. Heineman, *Chem. Soc. Rev.* **2010**, *39*, 1747–1763.
[65] M. J. Buono, N. V. L. Lee, P. W. Miller, *J. Physiol. Sci.* **2010**, *60*, 103–107.
[66] R. A. Robergs, F. Ghiasvand, D. Parker, *Am. J. Physiol-Reg. I* **2004**, *287*, R502–R516.
[67] W. Jia, A. J. Bandodkar, G. Valdes-Ramirez, J. R. Windmiller, Z. Yang, J. Ramirez, G. Chan, J. Wang, *Anal. Chem.* **2013**, *85*, 6553–6560.
[68] Y. H. Lee, J. S. Kim, J. Noh, I. Lee, H. J. Kim, S. Choi, J. Seo, S. Jeon, T. S. Kim, J. Y. Lee, J. W. Choi, *Nano Lett.* **2013**, *13*, 5753–5761.
[69] J. H. Lee, K. Y. Lee, M. K. Gupta, T. Y. Kim, D. Y. Lee, J. Oh, C. Ryu, W. J. Yoo, C. Y. Kang, S. J. Yoon, J. B. Yoo, S. W. Kim, *Adv. Mater.* **2014**, *26*, 765–769.
[70] J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. L. Liu, Z. L. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 1683–1687.
[71] P. P. Mercier, A. C. Lysaght, S. Bandyopadhyay, A. P. Chandrakasan, K. M. Stankovic, *Nat. Biotech.* **2012**, *30*, 1240–1243.
[72] L. Halamkova, J. Halamek, V. Bocharova, A. Szczupak, L. Alfonta, E. Katz, *J. Am. Chem. Soc.* **2012**, *134*, 5040–5043.
[73] A. Zebda, C. Gondran, A. Le Goff, M. Holzinger, P. Cinquin, S. Cosnier, *Nat. Commun.* **2011**, *2*, 370.
[74] M. T. Meredith, S. D. Minteer, *Annu. Rev. Anal.Chem.* **2012**, *5*, 157–179.
[75] S. C. Barton, J. Gallaway, P. Atanassov, *Chem. Rev.* **2004**, *104*, 4867–4886.
[76] E. Katz, K. MacVittie, *Energ. Environ. Sci.* **2013**, *6*, 2791–2803.
[77] N. Mano, F. Mao, A. Heller, *J. Am. Chem. Soc.* **2003**, *125*, 6588–6594.
[78] M. Rasmussen, R. E. Ritzmann, I. Lee, A. J. Pollack, D. Scherson, *J. Am. Chem. Soc.* **2012**, *134*, 1458–1460.
[79] K. MacVittie, J. Halamek, L. Halamkova, M. Southcott, W. D. Jemison, R. Lobeld, E. Katz, *Energ. Environ. Sci.* **2013**, *6*, 81–86.
[80] A. Szczupak, J. Halamek, L. Halamkova, V. Bocharova, L. Alfonta, E. Katz, *Energ. Environ. Sci.* **2012**, *5*, 8891–8895.
[81] L. Halamkova, J. Halamek, V. Bocharova, A. Szczupak, L. Alfonta, E. Katz, *J. Am. Chem. Soc.* **2012**, *134*, 5040–5043.
[82] W. Jia, G. Valdes-Ramirez, A. J. Bandodkar, J. R. Windmiller, J. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 7233–7236.
[83] G. M. Zhou, F. Li, H. M. Cheng, *Energ. Environ. Sci.* **2014**, *7*, 1307–1338.
[84] S. Berchmans, A. J. Bandodkar, W. Jia, J. Ramírez, Y. S. Meng, J. Wang, *J. Mater. Chem. A* **2014**, *2*, 15788–15795.
[85] J. Kim, W. R. de Araujo, I. A. Samek, A. J. Bandodkar, W. Jia, B. Brunetti, T. R. L. C. Paixão, J. Wang, *Electrochem. Commun.* **2015**, *51*, 41–45.
[86] A. J. Bandodkar, W. Jia, C. Yardımcı, X. Wang, J. Ramírez, J. Wang, *Anal. Chem.*, DOI 10.1021/ac504300n, in press.

Received: September 24, 2014
Accepted: October 22, 2014
Published online: January 8, 2015