

Poster Abstracts: Monday

Direct Covalent Attachment of Ion-Selective PVC Membrane onto the Substrate for Improved Characteristics

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Solid-contact ion-selective electrodes (SC-ISEs) have demonstrated considerable potential in various fields such as environmental monitoring, bioanalytical measurements, and wearable sensors over the past decades. In recent works, conducting polymers including POT, PEDOT, and PPy have been widely used as ion-to-electron transducers for SC-ISEs, which significantly improve their ion response stability by preventing water layer formation. However, the reproducibility of standard potential (E^0) is still one of the most significant and common problems to be solved [1]. Otherwise, it is necessary to calibrate each electrode before use, which is not desired. □

To improve the E^0 reproducibility for SC-ISEs utilizing conducting polymer as transducers, various strategies have been employed, such as the prepolarization of the conducting polymer layer or outer coating methods. [2, 3] For instance, the Lindfors group achieved significant enhancement in E^0 reproducibility by prepolarizing the conducting polymer before the deposition of the polymer membrane cocktail [2]. Joon et al. improved the stability of the E^0 by simply adding an outer layer of silicone rubber, which also exhibited potential in reducing biofouling [3].

We present here a novel strategy by creating a direct covalent linkage between the ion-to-electron transducer layer and the ion-selective membrane layer using click reaction. Specifically, CuAAC-based click chemistry was employed to covalently attach a thin layer of PVC onto the transducer layer that is either directly functionalized with ion sensing components or followed by the deposition of a second PVC layer with ionophores, ion exchangers, and plasticizer either through spin coating and drop-casting.

References:

1. Shao, Y., Y. Ying, and J. Ping, Recent advances in solid-contact ion-selective electrodes: functional materials, transduction mechanisms, and development trends. *Chem Soc Rev*, **2020**. 49(13), 4405-4465.
2. He, N., et al., Pre-Polarized Hydrophobic Conducting Polymer Solid-Contact Ion-Selective Electrodes with Improved Potential Reproducibility. *Anal Chem*, **2017**. 89(4), 2598-2605.
3. Joon, N.K., et al., PVC-Based Ion-Selective Electrodes with a Silicone Rubber Outer Coating with Improved Analytical Performance. *Anal Chem*, **2019**. 91(16), 10524-10531.

Self-Powered Smart Potentiometric Sensor with Relational Operation Function

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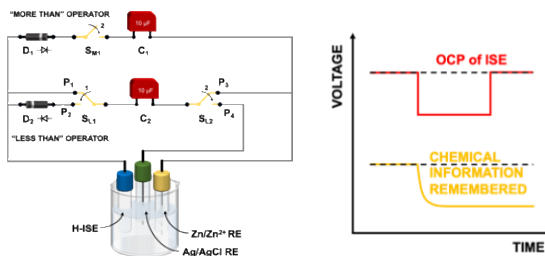
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Potentiometric sensor gives spontaneous voltage response to the ion concentration perturbation in the sample solution, this property makes potentiometric sensor an ideal signal source for the self-powered sensor. The previous works from our group have demonstrated that this voltage signal may be harvested and stored by a capacitor connected in serial with the electrodes. This voltage signal can be readout latterly with a simple multimeter.

Based on this, in 2021, our group proposed the first type of self-powered potentiometric sensor with memory. We put a diode in serial with one capacitor in the circuit, with this design, only the positive voltage change may be recorded in the capacitor for the later readout in the end of the measurement. A Zn/Zn²⁺ electrode was used as the reference electrode (RE) to overcome the forward voltage at hundreds of millivolts level. Comparing with the conventional Ag/AgCl electrode, the EMF of the ion-selective electrode (ISE) against the Zn RE has been lifted for about 1V, which is sufficient to charge the capacitor with a diode put in serial. However, this sensor can only record the voltage derivation in positive direction, the voltage change in the other direction cannot be remembered because of the single direction conductivity of the diode.

In this work, we constructed a self-powered sensor which is capable of recording both positive and negative voltage fluctuation during a period of few hours for the later readout. Capacitor C₁ and diode D₁ is connected to ISE and Zn RE as figure below illustrated for recording the positive voltage change. To record the negative voltage change, the capacitor was firstly charged by the ISE and the Zn RE, after the charging is finished, the Switch S_{L1} was placed to position P₂ to add the diode into the circuit. At the beginning moment of, the switch S_{L2} was moved from position P₃ to P₄ to generate a voltage drop about 1V across the capacitor C₂, this voltage drop will be used to overcome the forward voltage cross the voltage D₂, the further voltage decreasing from the ISE would be then recorded on the capacitor C₂.

In summary, this work demonstrated a new type of self-powered sensor which can record the voltage perturbation over a period of hours. This sensor may deploy as an affordable alternative option to monitor chemical information in the field of agriculture, aquaculture, etc.



Efficient Thiol-Click Reaction for the Study and Application of an Anion-Selective Electrode and pH Electrode

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Ion-selective electrodes (ISEs) are membrane potential sensors that respond to specific ions^[1] and find extensive applications in fields such as medicine^[2], biological research, and environmental monitoring. Leveraging the advantages of click chemistry, which is known for its convenience, efficiency, selectivity, and mild reaction conditions^[3], this study employs thiol-click reactions to construct a high-molecular-weight crosslinked network. Subsequently, this network is utilized for the preparation of ion-selective electrode membranes.

This study utilizes polypropylene or polyethylene-based films as support materials, epoxy resin or alkenes, and thiol compounds as cross-linking agents, and quaternary ammonium salts to provide anion exchange sites. This results in the preparation of structurally stable anion-selective membranes. The optimization of the composition yields an electrode membrane with a Nernstian slope of -56.3 mV/decade. Further characterization of the electrode membrane was carried out using FT-IR. By replacing the quaternary ammonium salt in the mixed solution with a cation exchange reagent, the electrode membrane exhibits responsiveness to hydrogen ions. In summary, this work aims to enhance the performance of chloride ion-selective electrodes and pH electrodes. The introduction of the thiol-click reaction brings certain advantages and promising prospects.

References:

1. E. Bakker, P. Bühlmann, and E. Pretsch, Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics. *Chemical Reviews*, **1997**. 97, 3083-132.
2. H. Dong, L. Zhang, W. Liu, and Y. Tian, Label-free electrochemical biosensor for monitoring of chloride ion in an animal model of Alzheimer's disease. *ACS Chemical Neuroscience*, **2017**. 8, 339-46.
3. C.E. Hoyle, T.Y. Lee, and T. Roper, Thiol-enes: Chemistry of the past with promise for the future. *Journal of Polymer Science Part A: Polymer Chemistry*, **2004**. 42, 5301-38.

Simple Systems for Electrochemical Ion Sensing

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Over a decade ago paper-based devices revolutionized the idea of Lab-on-a-chip systems, freeing them from the use of pumps, allowing easy and on chip sample pretreatment, sample mixing and storing of reagents [1,2]. The idea of simple systems goes beyond the use of paper, towards design of measurement setups, that are easier to use and prepare, cheaper and more versatile regardless the material used.

Here we would like to present two such systems for ion-sensing. First, presented in Fig. 1A allows for faster, and more stable measurements of ion-transfer at the classical polarizable interface, using reduced amount of reagents. By using a spectrophotometric cuvette and capillaries pulled from Pasteur pipettes we were able to prepare a 4-electrode cell, which uses few hundred microliters instead of 5-10 mL of each of the phases. Smaller interface allows to stabilize the signal faster, and reduced volume can be explored towards analysis of new recognition molecules. In this case we have tested several organoboron compounds as ionophores enabling detection of fluorine.

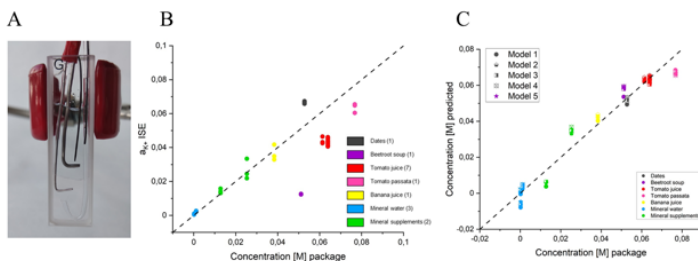


Fig. 1 A. Simple cell for 4-electrode experiments at the interface of two immiscible solutions, B. real vs. measured amount of potassium quantified using a single low-cost sensor C. using a low-cost electronic tongue setup.

Setups for voltammetric sensing of ions just as the one presented above are still not popular around the scientific community and ion-sensing is primarily accomplished through potentiometry. We have prepared low-cost ion-selective potentiometric electrodes using syringes and applied them to measure potassium in different food products, including pharmaceutical supplements, mineral water from a few brands, tomato juices from different brands, banana juice, dried fruits, tomato sauce, and a beetroot soup concentrate. Measurements agreed with the concentration calculated from the information given on the package for mineral water samples, pharmaceutical supplements, and banana juice. For other products the deviation reached up to 75% of the expected value (Fig.1B). To remediate this problem, we have constructed an electronic tongue-sensor array coupled with a machine-learning algorithm based on the original low-cost potassium electrode and additional sensors that could account for the different ionic compositions of the food products (Fig.1C).

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References:

1. W. Mazurkiewicz, M. Podrażka, E. Jarosińska, K.K. Valapil, M. Wiloch, M. Jönsson-Niedziółka, E. Witkowska Nery, *ChemElectroChem*, **2020**, 7, 2939–2956.
2. E. W. Nery, L. T. Kubota, *Anal Bioanal Chem*, **2013**, 405, 7573–7595.

Wafer Scale Fabrication of Miniaturized Ion Sensors for Healthcare Applications

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For healthcare applications, integrated miniaturized ion-selective sensors have shown their advantages in performing real-time multiplexed measurement in low sample volume [1]. Solid-contact ion-selective electrodes (ISEs) are a type of electrode which are made of a stack of a contact electrode, a transduction layer consisting of a conducting polymer, and a polymeric ion-selective membrane (ISM).

In our earlier work [2], a wafer scale process for fabrication of solid-contact ion-selective electrodes on a Si substrate was introduced, with the target application of measuring in bodily fluids such as blood and urine, starting with the ions Na^+ and K^+ [3]. In this work, we extend our sensor to Ca^{2+} , another key ion of interest in bodily fluids. For the calcium-selective membrane, we optimize the polymer/ionophore/lipophilic ion/solvent ratio to achieve the reported sensitivity and the final solution could still be dispensed in the glass wells. The wafer scale fabrication lets us test many devices and show good reproducibility. Here we show a calcium sensitivity of 28.4 mV/decade with a reproducibility of less than 4 % over 11 sensors, and a low limit of detection below 10^{-4} M. To demonstrate the long-term stability required for health applications we tested the sensor over several days. After 14-day storage in liquid, the sensor sensitivity remains above 24 mV/dec (Fig. 1). With this sensing platform, different ISEs can be tailored in a single chip by adding the corresponding ion-selective membranes for the desired ion, paving the way towards mass manufactured, multi-ion selective sensors.

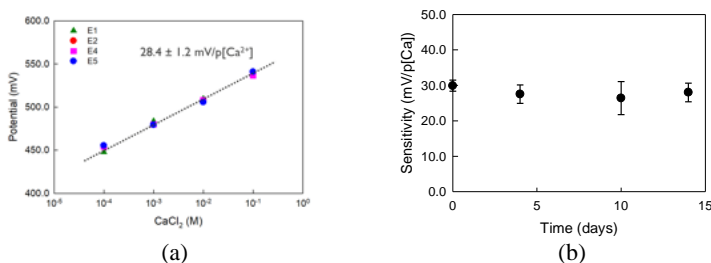


Figure 1: Linear dependence of electrode potentials of four calcium-selective electrodes on a single glass device on logarithm of the CaCl_2 concentration. A dotted line is a fit through the data for calculation of the sensitivity (a). Change in sensitivity of four calcium-selective electrodes over time stored in a solution containing 0.01 M CaCl_2 and 0.1 M KCl (b).

References:

1. J. Lee, M. C. Kim, I. Soltis, S. H. Lee, W. H. Yeo, Advances in Electrochemical Sensors for Detecting Analytes in Biofluids, *Adv. Sensor Res.* 2023, 2, 2200088.
2. V. A. T. Dam, M. A. G. Zevenbergen, Multi-ion sensor chip for healthcare applications, *Proc. Transducers 2023*, Kyoto, Japan, June, 2023.
3. K. Sharma et al., On-line monitoring of electrolytes in hemodialysis: on the road towards individualizing treatment, *Expert Rev. of Med. Dev.* 2016, 13, 933 – 943.

Ion-exchange and Lipophilicity Limitations of Ionic Liquid Reference Electrodes

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Reference electrodes (REs) based on moderately lipophilic electrolytes such as ionic liquids (ILs) offer an alternative to liquid junction reference electrodes together with opportunities for achieving integrated potentiometric sensing systems. However, before these tools could gain broader acceptance it is important to recognize and study their limitations. While some reports have suggested poor lifetimes and even incompatibility with classical ISEs [1], the connection between the lipophilicity of the used IL and the RE potential stability and resilience to lipophilic interferences remains insufficiently understood.

Herein we explore the working limits of REs based on polymeric reference membranes incorporating ILs. A theoretical framework is developed to describe the failure of REs in the presence of lipophilic solution ions [2]. The critical concentration at which the RE potential begins to deviate noticeably from its equilibrium value is estimated as the intersection of the separate Nernstian responses to the IL and the solution ion (Fig. 1). Furthermore, reference membrane lifetimes are assessed based on the IL partition constants acquired for the sensing matrix used in this study. Lastly, we discuss the effectiveness of potential stabilization with highly lipophilic electrolytes to establish the optimal range of IL lipophilicity for RE design.

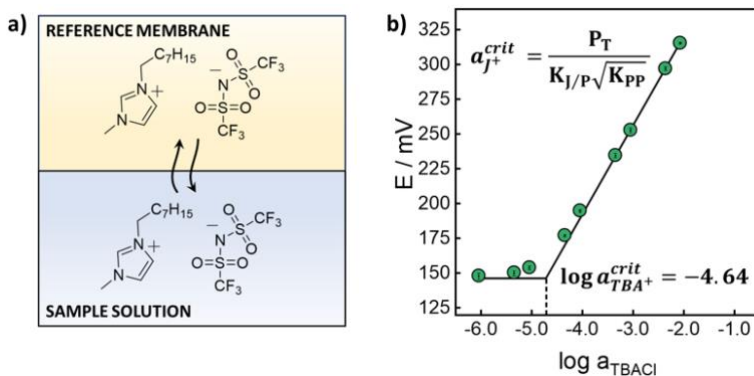


Figure 1. a) Partitioning of the ionic liquid $[C_8mim^+][C_1C_1N^-]$ between the electrode membrane and the sample solution and b) the response of the corresponding REs in the presence of different concentrations of tetrabutylammonium chloride (TBACl).

References:

1. M.P.S. Mousavi, M.K. Abd El-Rahman, E.K.W. Tan, H.H. Sigurslid, N. Arkan, J.S. Lane, G.M. Whitesides, Ionic liquid-based reference electrodes for miniaturized ion sensors: What can go wrong? *Sensors Actuators, B Chem.* **2019**, *301*, 127112.
2. N. Y. Tiuftiakov, E. Zdrachek, E. Bakker, Ion-exchange and Lipophilicity Limitations of Ionic Liquid Reference Electrodes. *Sensors Actuators, B Chem.* **2024**, *407*, 135474.

Tailoring the Response of Polymeric Optical Sensors for Individual Ionic Activities by Varying the Composition of their Sensing Layer

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While conventional polymeric optodes are attractive from a practical standpoint, they typically respond to the activity of two ions simultaneously. However, it has been shown that by adding a moderately lipophilic organic electrolyte (MLOE) to the membrane, sensitivity to an individual ionic activity can be achieved within certain limits [1, 2]. This results from the distribution of MLOE between phases, which stabilizes the interfacial potential [3].

This contribution develops the approach described in [2] and explores the effect of MLOE, chromoionophore and ionophore nature on the optode response to individual ionic activity. The response of optodes containing THexABArF^{*} and TOctABArF^{*} as MLOE and various chromoionophores and ionophores was studied spectrophotometrically and by means of digital colorimetry over a wide range of pH and electrolyte concentrations (Fig. 1). Replacing the chromoionophore caused a shift in the response median in accordance with its acidity (Fig. 1B). In contrast to conventional sensors, changing an ionophore had a negligible effect on the response range. (Fig. 1C). The obtained experimental results were evaluated in terms of the theoretical model described in [2].

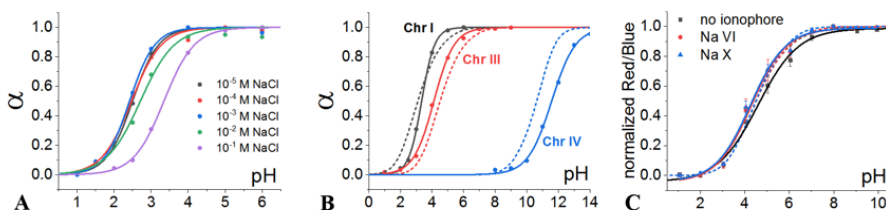


Figure 1. A: pH-response of (Chr I, NaVI, TOctABArF)-based optode at different Na⁺ concentrations. B, C: pH-response of optical sensors containing B) different chromoionophores and C) different ionophores. Concentration of background electrolyte $C_{\text{NaCl}} = 0.1$ M. Dashed lines: predicted response [2].

The observed patterns allow tuning the pH response range of MLOE-based optodes by varying the nature of the active components. By normalizing the optical readings of conventional optodes to the pH values obtained with the developed cation-independent pH optode, individual cation activities can be assessed.

*tetrahexylammonium and tetraoctylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

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References:

1. A.E. Stashkova, M.A. Peshkova, K.N. Mikhelson, Single-ion activity: Optical sensing vs. electrochemical sensing, *Sens. Actuators B: Chem.* **2015**, 207, 346–350.
2. N. V. Pokhvisheva, I.S. Prozherin, A. V. Kalinichev, M.A. Peshkova, Response Patterns of Chromoionophore-Based Bulk Optodes Containing Lipophilic Electrolytes: Toward Background-Independent pH-Sensing, *ACS Sensors* **2023**, 8, 3086–3094
3. A. Vincze, G. Horvai, The design of reference electrodes without liquid junction, *Electrochemical Society Proceedings* **1997**, 97-19, 550–555.

Constant Potential Coulometry for Ion-Selective Electrodes at Zero Current

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Constant potential coulometry for solid-contact ion-selective electrodes was introduced for the first time at this very conference by Prof. Johan Bobacka. As the name implies, a constant potential is applied between the ion-selective electrode (ISE) and reference electrode (RE). Thus, any phase boundary potential change at the ISE induces an opposite potential change on the capacitive transducing layer and gives rise to a transient current. The charge is obtained by integration of the current and an increased sensitivity is achieved compared to the classical Nernstian response.

Since then, the method has been applied to different ion sensing applications and gradually improved by (i) replacing the transducing layer with an electronically controlled electronic capacitor [1] and (ii) using an inverted electrode configuration to minimize signal drift [2]. A disadvantage of these approaches is that they require a transient current to pass through the measurement cell, which may introduce measurement errors and excludes the use of high impedance ISEs such as pH glass electrodes.

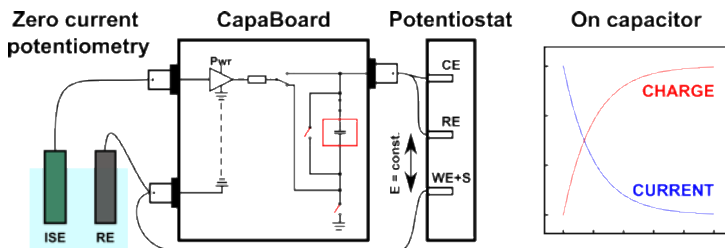


Figure 1. Scheme of the novel experimental setup for constant potential coulometry.

We present here, an electronic circuit that overcomes these limitations through the combination of (i) zero-current measurement at the ISE and (ii) a high-impedance input voltage follower [3]. As the transient current no longer flows through the ISE, its potential is left untouched and the need for a counter electrode (CE) is eliminated. The proposed setup is evaluated for chloride sensing as a model system and compared to zero current potentiometry. The procedure is then successfully applied with a glass electrode (i) to narrow pH ranges comparable to the values found in environmental samples with 0.01 pH steps (64 μ pH precision) and (ii) to a wider range of pH (4 to 10) with 1 pH steps to assess the versatility of the proposed method.

References:

1. P. Kraikaew, S. K. Sailapu, E. Bakker, Electronic Control of Constant Potential Capacitive Readout of Ion-Selective Electrodes for High Precision Sensing. *Sens. Actuators B Chem.* **2021**, 344, 130282.
2. R. Nussbaum, A. Nonis, S. Jeanneret, T. Cherubini, E. Bakker, Ultrasensitive Sensing of pH and Fluoride with Enhanced Constant Potential Coulometry at Membrane Electrodes. *Sens. Actuators B Chem.*, **2023**, 392, 134101.
3. R. Nussbaum, S. Jeanneret, E. Bakker, Increasing the Sensitivity of pH Glass Electrodes with Constant Potential Coulometry at Zero Current. *Anal. Chem.*, **2024**, in press.

Lipophilicity Criteria for Ionic Liquids Used in Liquid Junction Free Reference Electrodes

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The practical implementation of potentiometric cells with liquid junction free reference electrodes (LJFREs) is of paramount importance for the development of modern potentiometry, primarily from the point of view of creating compact and low-cost multisensor arrays using planar technologies. In this regard, reference electrodes based on ionic liquids introduced into a plasticized polymer membrane, the manufacturing technique of which is the same as in the case of indicator electrodes, are very attractive. However, despite intensive research conducted by leading scientific groups, LJFREs have not yet found widespread use. In particular, one of the key problems is the substantiation of the criteria for the lipophilicity of the components of the ionic liquid (IL) or hydrophobic salt (HS) used in relation to the composition of the solution under study. Here we present the results of our research on this problem, which boil down to the following.

1. The lower limit of lipophilicity IL or HS Q^+B^- is attributed to lifetime and the influence of IL components on the potential of the indicator electrode and can be easily estimated within the framework of known diffusion models. For example, in order for the potential deviation of the indicator electrode not to exceed 1 mV, the following conditions must be met: $C_{QB} < 0.04C_{IX}$, $C_{QB} < 0.04\overline{C_R^{tot}}/q$, where C_{QB} is IL concentration in the teste solution, q is the generalized diffusion parameter, described by the equation: $q = (D_m \cdot d_{aq}) / (D_{aq} \cdot d_m)$ depends on the plasticizer to polymer ratio and the rate of stirring.

2. The deviation of the LJFRE potential in the test solution containing ions I^+ , X^- is mainly due to changes in the concentration of Q^+ , B^- ions in the near-electrode layer of the solution. In order for the deviation not to exceed 1 mV, the following conditions must be met:

$$k_I \cdot k_B < \frac{0.04}{q} \cdot \frac{\overline{C_{QB}^{tot}}}{C_{IX}}, k_X \cdot k_Q < \frac{0.04}{q} \cdot \frac{\overline{C_{QB}^{tot}}}{C_{IX}}; \log(k_Q \cdot k_B) < 2\log \frac{0.04}{q} + \log \frac{\overline{C_{QB}^{tot}}}{C_{IX}} - \log(k_I \cdot k_X).$$

The first two conditions are necessary and sufficient if they are satisfied simultaneously. The last condition is necessary, but not sufficient. From the above conditions it follows that in addition to the lower limit of the lipophilicity of the IL, set by the criteria of lifetime and the absence of influence on the potential of the indicator electrode, there is also an upper limit of lipophilicity, which decreases with increasing lipophilicity of the electrolyte of the solution under study. From the obtained conditions it also follows that “symmetrical” ILs, characterized by approximately the same lipophilicity of the cation and anion, have limited applicability in electrolyte solutions in which the lipophilicities of the cation and anion differ greatly. In such cases, it is preferable to use “asymmetric” ILs, with the predominant lipophilicity of the cation or anion, respectively. The results obtained are confirmed by experimental data.

The influence of the nature of the IL components, in particular, their tendency to form ion pairs, and diffusion coefficients in the membrane phase on the acceptable limits of lipophilicity is also discussed.

Comparative Study of Potassium Ion-selective Electrodes with a Solid Contact. Temperature Resistance of Electrodes Depending on the Type of Solid Contact Material.

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Solid contact ion-selective electrodes (SCISEs) are useful and often chosen measuring devices in potentiometry. Due to their numerous advantages, they have begun to replace classic liquid-contact ion-selective electrodes. Not only measurement, storage and transport are simplified, but also the parameters of these electrodes, i.e. detection limit, lifetime or sensitivity, have improved greatly. However, the lack of an internal electrolyte has made the charge transfer of ions and their conversion to electron charge much more difficult, which in turn has caused a degradation in reversibility and potential stability. For this reason, it is important to improve their design so that the results are more accurate, precise and reproducible. One of the more commonly modified components of these electrodes is the solid contact (SC), which ensures the stability and reversibility of the potential [1,2]. In addition, it provides good ion-electron conductivity, faster charge transfer, which in turn improves other analytical parameters of the electrodes, i.e. membrane resistance and double layer capacity [3]. It is also important to check whether the material used to modify the design of our electrode fulfills its function under different environmental conditions such as temperature.

In order to test how temperature affects ion-selective electrodes modified with different intermediate layers, five electrode variants were made. The first ISE was based on an unmodified glassy carbon electrode, which acted as a control electrode. The other inner electrodes were sequentially modified with conductive polymers - perinone polymer B4 (layer applied in 10 cycles by cyclic voltammetry) and poly(3-octylthiophene) (POT) (layer applied by dosing an appropriate volume on the electrode contact). In addition, multi-walled carbon nanotubes (MWCNTs) and copper oxide nanoparticles (CuONPs) were used as a mediation layer as well, which were applied to the electrode substrate just like POT. The last type of sensors were SCISEs modified with a nanocomposite consisting of MWCNTs and CuONPs, and all electrodes were coated with an ion-sensitive membrane that provided them with selectivity to potassium ions. For all the prepared SCISEs, the effect of temperature on parameters such as the slope of the characteristics, the range of linearity, the limit of detection, the stability and reversibility of the potential, and the selectivity towards Mg^{2+} , Na^+ , Ca^{2+} ions was studied.

References:

1. J. Hu, A. Stein, P. Bühlmann, Rational design of all-solid-state ion-selective electrodes and reference electrodes. *TrAC Trace in Analytical Chemistry* **2016**, 76, 102-114.
2. C. Wardak, K. Pietrzak, K. Morawska, M. Grabarczyk, Ion-Selective Electrodes with Solid Contact Based on Composite Materials: A review. *Sensors* **2023**, 23, 5839.
3. Y. Lyu, S. Gan, Y. Bao, L. Zhong, J. Xu, W. Wang, Z. Liu, Y. Ma, G. Yang, L. Niu, Solid-Contact Ion-Selective Electrodes: Response Mechanism Transducer Materials and Wearable Sensors. *Membranes* **2020**, 10, 128.

Transfer of Hydrophobic Ions Between Immiscible Liquids at the Three-Phase Junction Using a Squaramide Ion Pair Receptor

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Although ion transfer between two immiscible electrolyte solutions (ITIES) is an excellent tool for label-free detection of a large number of various analytes, also not redox active molecules, its application is practically impossible for the detection of highly hydrophilic ions such as fluoride or sulfate.

We show that we can detect the transfer of sulfate and fluoride ions at a three-phase junction in a regular electrochemical cell, with a small organic drop deposited onto the surface of a glassy carbon electrode[1]. The transfer of ions facilitated by the presence of a novel ionophore in the organic phase. We investigated the properties of a specially synthesized ionophore, which should facilitate the transfer of sulfate ions (Fig 1.). The ionophore is one of a class of compounds that are built from three parts. The first part is an electron-deficient phenyl ring connected to a crown ether that binds cations, mainly potassium and sodium. The second part is the anion-binding domain, directly related to the cation-binding domain. The third part of the ionophore is a pentafluorophenyl group that imparts lipophilicity and provides acidity to the anion-binding domain. Both the first and third part can be exchanged for other functionalities. We evaluate the ionophore for transfer of sulfate ions and its selectivity towards other anions and test its application in a potentiometric setup.

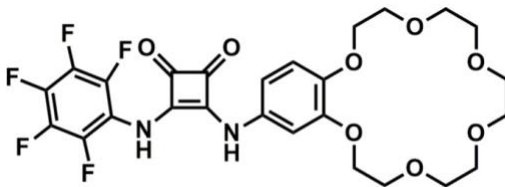


Fig 1. Structure of the evaluated ionophore [2].

References:

- [1] M. Podrażka, J. Maciejewska, W. Adamiak, E. Witkowska Nery, M. Jönsson-Niedziółka, Facilitated cation transfer at a three-phase junction and its applicability for ionophore evaluation, *Electrochimica Acta* 307 (2019) 326–333. <https://doi.org/10.1016/j.electacta.2019.03.201>.
- [2] M. Zaleskaya, M. Karbarz, M. Wilczek, Ł. Dobrzycki, J. Romański, Cooperative Transport and Selective Extraction of Sulfates by a Squaramide-Based Ion Pair Receptor: A Case of Adaptable Selectivity, *Inorg. Chem.* 59 (2020) 13749–13759. <https://doi.org/10.1021/acs.inorgchem.0c02114>.

Towards Mass-Production of Ion-selective Electrodes: Optimization of Membrane Composition and Novel Water Layer Stability Testing

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Solid-contact ion-selective electrodes have emerged as powerful tools enabling miniaturization and integration in portable devices for point-of-care applications [1]. High device-to-device reproducibility, extended lifetime and minimal calibration requirements provide accurate laboratory-level test results with minimal hurdles for the end consumer. Fast, high-throughput, low-cost, environmentally conscious production of such devices is of critical importance. While mass production of electrical contacts is currently dominated by screen-printing [2], large-scale deposition of ion-selective membranes in a reproducible manner is still challenging, owing to the physical properties of commonly used solvent-cast membranes and the costs of utilized membrane components.

Presented here is the optimisation of ion-selective membrane composition that enables precise, reproducible and fast deposition using a fluid dispenser aimed towards industrial production. A “blank” membrane containing only poly(vinyl chloride) (PVC) and a plasticizer was prepared in a solvent mixture of tetrahydrofuran and cyclohexanone. Different solvent ratios were tested to increase the boiling point of the solvent mixture and to minimize the undesirable coffee-ring effect of the deposited membrane. The amount, morphology and precision of the depositions were probed by the colorimetric absorbance method [3]. The deposited volume required to obtain a theoretical response to tetrabutylammonium ions was optimized using ion-exchanging membranes containing only PVC, plasticizer and potassium tetrakis(4-chlorophenyl)borate (KTCIPB) deposited onto screen-printed carbon electrodes. Potassium-selective membranes were spotted and calibrated in standard solutions of KCl, giving a slightly sub-Nernstian response of 54.2 mV/dec, with a standard deviation of E^0 value of 5.5 mV ($n=7$) without any conditioning.

A novel experimental setup is designed to test the operational stability of the proposed sensors, which probes for the potential change when one membrane electrode is exposed to the sample while a second connected membrane is kept dry. This allows one to identify the effect of sample introduction on the underlying ion to electron transducer layer.

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References:

1. J. Hu, A. Stein, P. Bühlmann, Rational design of all-solid-state ion-selective electrodes and reference electrodes, *Trends in Analytical Chemistry* **2016**, 76, 102–14.
2. A. Hayat, J.L. Marty, Disposable Screen Printed Electrochemical Sensors: Tools for Environmental Monitoring, *Sensors* **2014**, 14(6), 10432–53.
3. Y. Soda, K.J. Robinson, T.J. Cherubini, E. Bakker, *Lab Chip* **2020**, 1441–48.

A simple and Sensitive Method for Ga(III) Determination Using a Friendly Electrochemical Sensor

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The interest in the determination of Ga(III) has been very high for many years and has not weakened. This is due to its wide application in various fields. Formerly used in thermometers, gallium compounds are now used in LEDs, lasers, the manufacture of solders and low-melting alloys, but also in illusionists' tricks. Such widespread use of gallium compounds is associated with an increased potential for their release into the environment. The effects of gallium compound poisoning can include skin rashes, rapid heartbeat, shortness of breath, dizziness and headaches. However, the toxicity of gallium is relatively low compared to the many uses of gallium compounds. Nevertheless, environmental monitoring is necessary to determine even trace concentrations of gallium in various types of samples, including water samples [1,2].

The method we used to determine gallium, with a detection limit of 9.5×10^{-10} mol L⁻¹, was adsorptive stripping voltammetry. The measurements were carried out using multiwall carbon nanotubes/spherical glassy carbon (MWCNTs/SGC) electrode modified with a lead film. In the proposed method, gallium was accumulated on the surface of the lead film formed on the working electrode in the form of a Ga(III)–cupferron complex. In the second step, the voltammetric signal was recorded. The next step was to change the potential from –0.7 V to –1.2 V, which resulted in reducing gallium from the cupferron complex. A peak at a potential of –0.9 V appeared on the voltammogram, which is the basis for the quantitative analysis of Ga(III) in the proposed procedure. The developed method was applied to determine gallium in real samples such as Bystrzyca river water and tap water after enrichment with Ga(III) ions. The recovery values were obtained in the range of 95.3 to 104.9% with a standard deviation in the range of 4.6 to 6.2%, confirming the correctness of the proposed method and demonstrating its suitability for the determination of Ga(III) in environmental water samples [3].

References:

1. C. R. Chitambar, Medical applications and toxicities of gallium compounds. *International Journal of Environmental Research and Public Health* **2010**, *7*, 2337–2361.
2. S. Pysarevska, L. Dubenska, The advances in electrochemical determination of gallium (III). *Chemistry of Metals and Alloys* **2018**, *11*, 34–41.
3. M. Grabarczyk, M. Fiałek, E. Wlazłowska, Multiwall carbon nanotubes/spherical glassy carbon as environmentally friendly adsorption materials utilized in adsorptive stripping voltammetry for the determination of trace amounts of Ga(III). *Materials* **2024**, *17*, 966.

Towards Rational Design of Ion-Selective Electrode Arrays for Environmental Applications: Is Bigger Really Better?

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Ion selective electrodes (ISEs) have many desirable characteristics for in-situ environmental measurements, such as relatively low cost, power demand, and size, and a lack of consumable reagents. One transformative application is nitrate sensors for estuarine and coastal environments, where ISEs could offer drastically lower costs than state-of-the-art optical devices (~\$20k), thereby expanding the achievable spatiotemporal scale of nutrient measurements. However, current ionophores lack the specificity for quantifying micromolar levels of nitrate against the background of seawater, a common issue in complex, varying environmental matrices. Alternative approaches have been proposed, e.g. reducing salt background before measurements [1], but adoption remains limited, possibly due to limitations on sampling frequency and consumable life.

We instead take a direct approach with no sample preparation, using an ISE array coupled with machine learning models to correct for interferences and improve selectivity. This approach can reduce error [2] and decrease limit of detection (LOD) [3] in complex matrices compared to conventional calibrations. Redundant sensors of the same chemistry can also improve precision near the LOD [4]. Many authors suggest larger and more diverse arrays may yield better results, but to our knowledge no exhaustive study has been published. We aim to develop a rational framework for ISE array design by systematically investigating how the number of unique and replicate sensors affects analytical performance.

As a demonstration, we develop an ISE array to measure nitrate in seawater because of the potential impact and because the high number of dissolved constituents may necessitate many sensing elements. We will present our hardware platform for designing large ISE arrays as well as our experimental design and preliminary results. The setup consists of customizable screen-printed arrays, 128-channel data acquisition circuitry, and a sequential injection analysis (SIA) system capable of generating solutions with up to 20 independently-variable components. Several machine learning models will be evaluated on a test set structured for end-user relevant LOD and accuracy quantification, and predictor pruning used to optimize the number of sensors. Heatmaps will identify which sensors are most important, and correlations with sensor characteristics (i.e. selectivity coefficients) will be reported.

References:

1. M. Cuartero, G. A. Crespo, and E. Bakker, "Tandem Electrochemical Desalination–Potentiometric Nitrate Sensing for Seawater Analysis," *Anal. Chem.* **2015**, 87, 8084–8089
2. M. Gutiérrez, S. Alegret, R. Cáceres, J. Casadesús, O. Marfà, and M. Del Valle, "Application of a potentiometric electronic tongue to fertigation strategy in greenhouse cultivation," *Comput. Electron. Agric.* **2007**, 57, 2–22.
3. A. Mimendia, A. Legin, A. Merkoçi, and M. del Valle, "Use of Sequential Injection Analysis to construct a potentiometric electronic tongue: Application to the multidermination of heavy metals," *Sens. Actuators B Chem.* **2010**, 146, 420–426.
4. P. W. Dillingham, T. Radu, D. Diamond, A. Radu, and C. M. McGraw, "Bayesian Methods for Ion Selective Electrodes," *Electroanalysis* **2012**, 24, 316–324.

A New Discovery about Potentiometric Stability of Ion-Selective Membrane: Impurities in Tetrahydrofuran

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Tetrahydrofuran (THF) is the most commonly used solvent for the preparation of modern ion-selective membranes (ISM). Until now, the influence of impurities in THF towards potentiometric instability of ion-selective membrane was associated with either presence of residual water [1] or probably the peroxides [2]. To address this issue, most literature recommends to re-distill THF prior to use in potentiometric membrane preparation [3]. Current study reveals that the actual THF impurity that is responsible for potential instability of ISM due to by-products from the oxidation of THF, which contains hydroxyl and carboxyl groups. These by-products with boiling point of above 200 °C result in residuals within the matrix of ISM. The density functional theory supports the pathway of autooxidation of THF, and the chemical structure from one of the uncertain impurities was predicted. The significant hydrophilicity of these impurities affects the partitioning of the ion sensing components in the membrane, enhancing the leaching of the membrane components from membrane phase and deteriorating the potential stability of the membrane. This finding explains why re-distillation of the aged THF is necessary to avoid unstable potentiometric signals from ion-selective membrane.

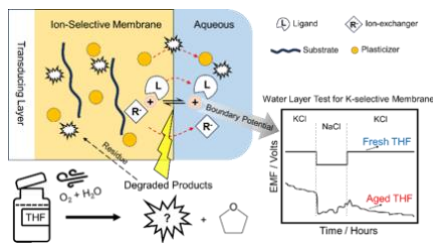


Figure 1. The degraded products in the aged THF influences the potentiometric stability of the solid-contact ion-selective electrode.

References:

1. Veder, J.-P.; De Marco, R.; Clarke, G.; Chester, R.; Nelson, A.; Prince, K.; Pretsch, E.; Bakker, E. *Anal. Chem.* **2008**, *80* (17), 6731–6740.
2. Gonçalves, A. R.; Ghica, M. E.; Brett, C. M. A. *Electrochimica Acta* **2011**, *56* (10), 3685–3692.
3. Püntener, M.; Fibbioli, M.; Bakker, E.; Pretsch, E. *Electroanalysis* **2002**, *14* (19–20), 1329–1338.

Visualization of Latent Fingerprints on Fired Cartridges Using Electrochemical Dye Deposition

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The visualization of fingerprints (FP) on metal substrates is a problematic issue in contemporary criminology [1]. This work is focused on the visualization of latent FP left on brass subjects, especially on cartridge cases (Fig. 1). The conditions for deposition of poly(neutral red) (PNR) from a neutral solution were optimized for possible preservation of genetic information while producing high-quality visualization of FP. Films of PNR were deposited by cyclic voltammetry (CV) onto working electrode, which was composed of a brass substrate with sebaceous FP. A stable, colored polymer film of PNR was formed onto brass substrate around the sebum after the polymerization. The thickness of the polymer layer is a crucial factor in getting clear and visible FP using polymer films and can be adjusted by controlling the number of deposition cycles. Another key factor to consider for a visualization is age and quality of the applied FP. A film of PNR deposited on the brass surface using the CV method visualized remains of prints on fired cartridges better (conditions: -200 – 500 mV (vs. Ag/AgCl), scan rate 50 mV/s, 4–5 cycles). A greater contrast between the print and the PNR film can be achieved by applying a solution of different pH. Surfaces after the electrochemical deposition of PNR were characterized optically, profilometrically, and spectroscopically. The suggested method of visualizing FP using polymer layers was confirmed to be applicable, gentle, and relatively fast compared to other methods.

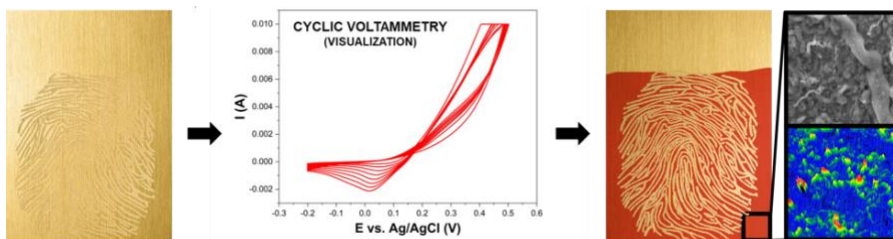


Fig. 1: Concept of the visualization of latent fingerprints left on brass subjects.

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References:

1. C. M. A. Girelli, B. J. M. Lobo, A. G. Cunha, J. C. C. Freitas, F. G. Emmerich, Comparison of practical techniques to develop latent fingermarks on fired and unfired cartridge cases. *Forensic Sci. Int.* **2015**, *250*, 17–26.

Poster Abstracts: Tuesday

A High-throughput Electrochemical Instrument for Single Entity Analysis

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High-throughput electrochemical measurements with high resolution at the single entity level for chemical or biochemical processes is a significant technique in precise diagnostic and detection, such as parallel DNA sequencing and protein recognition. The high-throughput of measurements with high accuracy depends on the advanced instrumentation, which has sub-picoampere level resolution, high bandwidth and parallel measurement channel. Currently, it is still a challenge for an instrument to have both of these features. Herein, we presented a multi-channel electrochemical instrument that integrates low-noise amplifier array and multi-channel digital circuit board. By using bandwidth compensation and multiplexers, our multi-channel instrument has over 100 kHz bandwidth and can simultaneously measure 16-channel current signals at ultra-low noise. The further experiments of single-molecule detection with an aerolysin nanopore and single Pt nanoparticle catalysis during the dynamic collision process has improved the instrument has been successfully applied in the detection of actual samples^[1,2].

References:

1. C. B. Zhong, H. Ma, J. J. Wang, L. L. Zhang, Y. L. Ying, R. Wang, Y. J. Wan, Y. T. Long. An ultra-low noise amplifier array system for high throughput single entity analysis. *Faraday Discuss.*, **2022**, 233, 33-43.
2. H. Ma, C. B. Zhong, Y. L. Ying, and Y. T. Long. Seeing is not believing: filtering effects on random nature in electrochemical measurements of single-entity collision. *ACS Meas. Sci. Au*, **2022**, 2 (4), 325-331.

Naphthopyran-Based Photoswitching with Phase-Sensitive Detection for High-Contrast Selective Imaging and Nanoscale Chemical Sensing

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Intensity-based fluorescence imaging and sensing commonly suffer from spectral overlap and optical background interference.[1] While fluorescence lifetime measurements in frequency domain offer an alternative, acquisition on the nanosecond level is largely constrained by sophisticated and high-cost equipment.[2, 3]

Here, we propose a category of photoswitchable nanoprobes (containing naphthopyran and a fluorescent donor) which is operated in phase-sensitive detection mode. With the photoswitching kinetics in the millisecond to second range, the frequency domain detection was accomplished with cost-effective equipment including a modulated light-emitting diode (LED) as light source and a common digital camera, offering an alternative to conventional fluorescence lifetime imaging. We demonstrate that the phase shift ($\Delta\phi$) of the sinusoidal fluorescence emission could be regulated by the molar ratio of fluorescent donor to naphthopyran in the nanoprobes. We also propose $\Delta\phi$ as a self-referencing quantity for high-contrast imaging of the nanoprobes and as dynamic signal readout in chemical sensing. Photoswitchable nanoprobes for protamine, a polycationic protein used as neutralizer of the anticoagulant heparin,[4] were demonstrated as an application.

References:

1. M.Y. Berezin and S. Achilefu, Fluorescence Lifetime Measurements and Biological Imaging. *Chemical Reviews*, **2010**. *110*, 2641-2684.
2. W. Becker, Fluorescence lifetime imaging – techniques and applications. *Journal of Microscopy*, **2012**. *247*, 119-136.
3. R. Liu, Z. Zhao, L. Zou, Q. Fang, L. Chen, A. Argento, and J.F. Lo, Compact, non-invasive frequency domain lifetime differentiation of collagens and elastin. *Sensors and Actuators B: Chemical*, **2015**. *219*, 283-293.
4. X. Xie, J. Zhai, G.A. Crespo, and E. Bakker, Ionophore-Based Ion-Selective Optical NanoSensors Operating in Exhaustive Sensing Mode. *Analytical Chemistry*, **2014**. *86*, 8770-8775.

Development of Paper-based Analytical Device for Point-of-care Nucleic Acid Quantification Combining CRISPR/Cas12a and Personal Glucose Meter

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Taking advantage of the low cost and wide availability of personal glucose meters (PGMs), methods combining the CRISPR/Cas system and PGMs for nucleic acid quantification have been reported for point-of-care testing (POCT). They rely on the conversion of the target nucleic acid concentration into a glucose signal through an enzymatic reaction. However, most reported assays require multi-step operations involving pipetting and separation [1].

In this work, we aimed at developing a paper-based biosensor for quantification of nucleic acids by combining the CRISPR/Cas system and PGMs. Pre-deposition of all required reagents on a multi-layer paper device enables assays to be performed by end-users without multiple operation steps and reagent handling. The device consists of three layers of wax-patterned paper (Fig. 1a). A target DNA-specific Cas12a-CRISPR RNA (crRNA) complex and single-stranded DNA-conjugated invertase immobilized on magnetic beads (MB probe) are deposited on the first layer, while sucrose is dried on the third layer. Application of a sample containing target DNA (tgDNA) activates the Cas12a-crRNA complex in the first layer, resulting in release of invertase through nonspecific trans-cleavage of ssDNA at the surface of the MB probe. After the cleavage reaction, removing a hydrophobic film separating the first and second paper layers allows the released invertase to flow through the second filter layer, while magnetic beads are retained. When reaching the third layer, the invertase converts the pre-deposited sucrose to glucose, which is subsequently detected by the PGM.

Through evaluation of factors including paper substrate, magnetic bead size, and reagent drying methods among others, a tgDNA concentration response was obtained from a single sample application (10 μ L) without any further user intervention except for the hydrophobic film removal and washing buffer application (Fig. 1b). For proof-of-concept, the detection of human papillomavirus-DNA (43 base pairs) has been achieved.

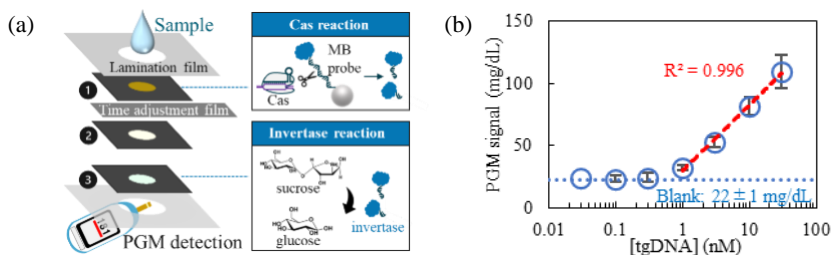


Fig. 1 (a) Design of the multi-layered paper-based device and its working principle; (b) Response curve for human papillomavirus-DNA obtained with the device within 30 minutes of total reaction time; error bars represent the mean values $\pm 1\sigma$ ($n = 3$).

References:

1. B. Fang, Z. Jia, C. Liu, K. Tu, M. Zhang, L. Zhang, A versatile CRISPR Cas12a-based point-of-care biosensor enabling convenient glucometer readout for ultrasensitive detection of pathogen nucleic acids. *Talanta* **2022**, *249*, 123657.

Fluorescent and Colorimetric RT-LAMP as a Rapid, Reliable, and Specific Qualitative Method for POCT

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Point-of-care testing (POCT), also known as near-patient testing or bedside testing, is a vital aspect of medical diagnostic testing that is applied directly at the site of need. This type of testing plays a significant role in the diagnosis and subsequent treatment of patients. In the context of the COVID-19 pandemic, POCT has been developed rapidly to improve speed, sensitivity, and ease of use compared to traditional methods like nucleic acid amplification tests (NAAT) and rapid antigen tests. Golden standard laboratory test for detecting active infections reverse transcription-polymerase chain reaction (RT-PCR) requires sophisticated equipment, skilled technicians, and long turnaround times. This all doesn't meet POCT requirements. To overcome these challenges, isothermal amplifications such as reverse transcription loop-mediated isothermal amplification (RT-LAMP) have become more popular, as they eliminate the temperature cycling step and simplify the process, making it faster, cost-effective, and energy-efficient. RT-LAMP is the most sensitive and specific of the isothermal amplification approaches, utilizing four to six primers that recognize six to eight different regions in the target nucleic acid molecule. Amplification is performed at a constant temperature between 60 °C to 65 °C, eliminating the need for thermal cycling and fluorescence monitoring, simplifying the process, and reducing dependence on complex equipment. RT-LAMP is an appropriate method for POCT and on-site testing scenarios where immediate results are critical for informed decision-making. RT-LAMP can be monitored in real-time by highly sensitive fluorescence or colorimetry. While fluorescence-based detectors can be complicated for POCT due to the general requirement for bulky and expensive fluorescence instruments, high background, and often inhibition of the amplification process due to the increased dye concentration, colorimetry is simpler and exposed to fewer cross-contamination risks. The color-change is caused by colorimetric indicators, which change color in response to pH shifts during amplification. This option is increasingly attractive for POC applications as it does not require complex equipment and optical modules. In this work, we demonstrate two versatile approaches for POC applications, utilizing fluorescence and colorimetric RT-LAMP analysis using specifically modified magnetic nanoparticles for sample preconcentration and nucleic acid isolation. These systems are highly sensitive, specific, and effective tools with potential in human and veterinary medicine.

Study of the Interaction of Lipopolysaccharides Incorporated in Lipid Vesicles with the Concanavalin A and DNA Aptamers Using QCM-D Method

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Lipopolysaccharides (LPS) incorporated into the outer membrane of bacteria can be considered as indicators of bacterial contamination in food samples [1]. For modeling of the bacterial pathogens, it can be useful to use lipid vesicles with incorporated LPS. One of the most dangerous foodborne pathogens is *Salmonella enterica* serotype typhimurium. In this work we prepared lipid vesicles with various weight fraction of LPS isolated from *Salmonella* in order to study their interaction with concanavalin A (ConA) or DNA aptamer layers at the gold surface using quartz crystal microbalance with dissipation monitoring (QCM-D). For this purpose the ConA or DNA aptamers specific to LPS have been covalently attached to the monolayers of 11-mercaptoundecanoic acid (MUA) [2]. Using QCM-D we monitored the formation of ConA or DNA layers. We have shown that optimal concentration of Con A for the lectin layers formation was 0.3 mg/mL and for DNA aptamers it was 1 μ M. Formation of both ConA and DNA layers have been accompanied by decrease of resonant frequency, f , and increase of dissipation, D . Considering that ConA formed relatively rigid layers we applied Sauerbrey equation for estimation of the surface density of the lectins, which was $1.13 \times 10^{12}/\text{cm}^2$. This value is similar to the $1.19 \times 10^{12}/\text{cm}^2$ that correspond to the maximum coverage of ConA [3]. We compared adsorption of lipid vesicles with different fraction of LPS and containing LPS from different bacteria. Vesicles containing 50 % LPS caused the most prominent decrease of the resonant frequency during interaction with ConA and aptamer layers. Using Kelvin-Voigt viscoelastic model and multiharmonic response of acoustic sensors we determined changes of viscoelastic values of the molecular layers during interaction of vesicles with ConA and aptamers.

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References:

1. A. Mobed, M. Hasanzadeh, Environmental protection based on the nanobiosensing of bacterial lipopolysaccharides (LPSs): material and method overview. *RSC Adv.*, **2022**, 12, 9704.
2. H. Yang, H. Zhou, H. Hao, Q. Gong, K. Nie, Detection of Escherichia coli with a label-free impedimetric biosensor based on lectin functionalized mixed self-assembled monolayer. *Sensors and Actuators B*, **2016**, 229, 297-304.
3. S.S. Wijetunge, J. Wen, Ch.K. Yeh, Y. Sun. Lectin-conjugated liposomes as biocompatible, bioadhesive drug carriers for the management of oral ulcerative lesions. *ASC Appl. Bio Mater*, **2018**, 1, 1487-1495.

The Potentiometric Response of Hydrophilic Ion-Exchanger Gold Nanopore-Based Membranes

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Permselective membranes are crucial to many applications that include ion-selective electrodes, energy conversion, and separation. Here, we present a detailed theoretical and experimental investigation of the potential response of hydrophilic ion-exchanger membranes that are based on gold nanopores functionalized with a thiol-bearing sulfonate derivative. In contrast with conventional polymer-based permselective membranes, we confirmed equal potential responses for cations of the same valency, including both inorganic and organic cations. A Poisson/Nernst-Planck (PNP) model [1], which was fitted to the potential response for monovalent ions, was shown to accurately predict the responses for higher valency cations, indicating that the sulfonate-decorated nanopores interact with all investigated ions in a largely electrostatic manner. The synthetic versatility of gold nanoporous membranes—in addition to the possibility of a PNP model-based rational design of their properties—makes such nanopore-based membranes a promising alternative to existent permselective membranes. The main advantage is the prompt on-demand synthesis of membranes with custom properties.

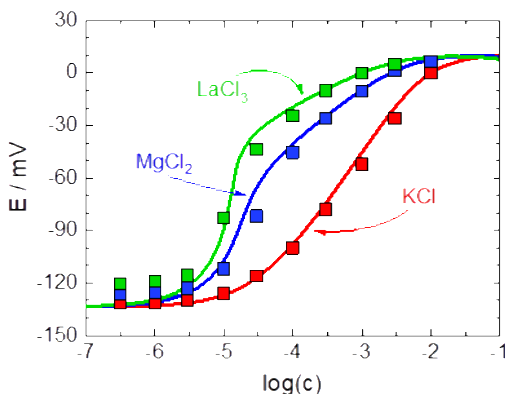


Figure 1. Measured (symbols) and simulated (lines) potential responses of 2-mercaptoethanesulfonate-modified membranes with 10-nm pores. The simulations used the same parameters for all ions, showing the predictive power of the PNP model.

References:

1. I. Makra, E. Jégerszki, L. Bitter, R. E. Gyurcsányi, Nernst-Planck/Poisson model for the potential response of permselective gold nanopores. *Electrochimica Acta* **2012**, *73*, 70-77.

Multisensor Platform for Non-Invasive Diagnosis of Early-Stage Esophageal Cancer

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Esophageal carcinoma (EC) is a serious malignant tumor and the sixth most common cause of cancer-related death despite being only the eighth most common type of cancer in the world [1]. The high mortality of EC compared to its incidence is attributed to the advanced stage of disease at the time of the initial diagnosis [2]. The prognosis is significantly better if the condition is detected early, but the diagnosis requires an unpleasant endoscopic examination and/or mucosa biopsies which discourages people in the risk group from taking part in regular screening. Therefore, developing a non-invasive test is critical.

In recent years, microRNAs (miRNA) have emerged as potential biomarkers for diagnosis, prognosis and therapy [3]. MicroRNAs are reported to be present in saliva and can be used to develop a non-invasive and early-stage test for esophageal cancer. Here, we propose a new low-cost sensor array platform for multiplex miRNA detection to demonstrate its utility with biomarkers of EC. Our approach utilizes p-nitrobenzene diazonium salts electrografted onto laser-induced graphene (LIG) electrodes. As a result of the electrochemical control over the reactions, grafted nitro groups can be sequentially reduced to amines and modified with capture probes using ‘click chemistry’ offering a simple way to fabricate the sensors functional layer. The LIG electrodes, which are fabricated directly from polymer films, can easily be incorporated into capillary-driven microfluidic systems.

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References:

1. D. J. Uhlenhopp, E. O. Then, T. Sunkara, and V. Gaduputi, “Epidemiology of esophageal cancer: update in global trends, etiology and risk factors,” *Clinical Journal of Gastroenterology*, **2020**, 13, 6, 1010–1021
2. K. J. Napier, M. Scheerer, and S. Misra, “Esophageal Cancer: A Review of Epidemiology, Pathogenesis, Staging Workup and Treatment Modalities,” *World J. Gastrointest. Oncol.*, **2014**, 6, 5, 112–120
3. L. Jamali *et al.*, “Circulating microRNAs as diagnostic and therapeutic biomarkers in gastric and esophageal cancers,” *J. Cell. Physiol.*, **2018**, 233, 11, 8538–8550

Visualizing Molecularly Imprinted Cavities in Electrically Insulating Polymer Nanofilms

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Molecularly imprinted polymers (MIPs) have been intensively studied as synthetic receptors for the selective recognition of ions, small molecules, and macromolecules. They can serve as robust alternatives to biological origin affinity reagents such as antibodies and can therefore be used in a wide range of applications, that includes drug delivery, affinity assays, separation and chemical sensing.[1] The advances in MIP synthesis offer unique advantages in terms of the control and reproducibility of the synthetic process. This is especially valid for the generation of highly affine and selective MIPs for protein recognition by using sophisticated surface and epitope imprinting methods along with mild synthetic conditions.

However, several fundamental assumptions of protein MIP synthesis remain without explicit and direct confirmation, in particular the physical presence and distribution of imprinted cavities for protein recognition. There are only indirect evidences for the formation and presence of such cavities, i.e. the selective binding of the target is accepted as confirmation of the formation of such binding sites. Obviously, the imaging of such molecular size cavities is already very difficult with the highest resolution imaging techniques (atomic force microscopy (AFM), SEM, etc.). This is particularly true for peptide epitope-imprinted polymers, where only a characteristic short peptide of the parent protein is used as a template instead of the whole protein. To this adds the difficulty of identifying cavities due to the molecular imprinting as even highly conformal polymer nanofilms are affected by the inherent roughness of the underlying electrode surface beside that of the polymer film.

Therefore, we aimed to develop a conductive AFM (cAFM) -based method to map the peptide and protein imprinted binding cavities in polymer nanofilms liberated after the template removal. Here we report a new cAFM method that can identify and determine the distributions of imprinted binding cavities after controlled gold deposition. The gold deposition forms gold nanowires in the imprinted cavities revealing their presence while the cAFM can confirm that these are contacted to the substrate electrode, i.e. can rule out contingent, non-specific gold nanoparticle deposition on the polymer surface.[2]

References:

1. Z. El-Schich, Y. Zhang, M. Feith, S. Beyer, L. Sternbæk, L. Ohlsson, M. Stollenwerk, A. G. Wingren, Molecularly imprinted polymers in biological applications. *Biotechniques*, **2020**, *69*, 6.
2. X. Zhang, A. T. Waffo, A. Yarman, N. Kovács, Z. Bognár, U. Wollenberger, I. M. El-Sherbiny, R. Y. A. Hassan, F. F. Bier, R. E. Gyurcsányi, I. Zebger, F. W. Scheller, How an ACE2 mimicking epitope-MIP nanofilm recognizes template-related peptides and the receptor binding domain of SARS-CoV-2. *Nanoscale*, **2022**, *14*, 18106-18114.

Zero-Current Chronopotentiometry with Wired Biosensors

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Glucose biosensors are extremely important for point of care measurements and one of the major applications of electroanalytical chemistry. These sensors often use amperometric detection methods in which a redox mediator is used to shuttle electron between the electrode and the enzyme reaction site. Heller et al. developed the “wired” biosensor where the redox mediators are bound to the polymer containing the enzyme, thereby providing a connection to the electrode surface. [1] To achieve selectivity and avoid interference, a permselective layer is normally deposited which will also limit the diffusion of the analyte to the enzyme. The sensor is then no longer governed by the enzyme turnover rate but by the analyte diffusion, resulting in some protection from variations in enzyme kinetics and enzyme degradation. [2] Unfortunately, these sensors are subject to signal drift, which was attributed by Damala et al. to the charging of the redox polymer through the oxidation/reduction of redox center not connected to the enzyme. [3] Passive detection methods at open circuit may overcome some of these limitations. Nagy et al. introduced a chronopotentiometric method based on the measurement of the open circuit potential (OCP) decay resulting from the reduction of an oxidized redox mediator adsorbed on the electrode by NADH in solution. They correlated the initial slope of the potential decay to the NADH concentration. [4]

In this work we propose a new chronopotentiometric time dependent readout for a “wired” glucose biosensor based on glucose oxidase. A two-step process involving the oxidation of the redox polymer (ferrocene-modified branched poly(ethylenimine)) followed by the monitoring of the OCP over time allows one to measure a transition time characteristic to the glucose concentration in solution. The transition time (t_r) corresponds to the potential jump due to the reduction of the previously oxidized ferrocene moieties by the electron generated by the enzyme converting glucose in gluconolactone. Thanks to an outer diffusion limiting membrane t_r is related to the concentration of glucose. Nafion and a blend of hydrophilic polyurethane and polyvinyl alcohol/vinyl butyral copolymer are used as outer permselective membrane to repel interference in phosphate buffered saline solutions and blood samples.

References:

1. A. Heller, Electrical wiring of redox enzymes, *Acc. Chem. Res.* **1990**, *23*, 5, 128-134.
2. J. H. Han et al., Glucose biosensor with a hydrophilic polyurethane (HPU) blended with polyvinyl alcohol/vinyl butyral copolymer (PVAB) outer membrane, *Sens. Actuators B Chem.* **2007**, *123*, 384-390.
3. P. Damala, N. Yu. Tiuftiakov, and E. Bakker, Avoiding Potential Pitfalls in Designing Wired Glucose Biosensors, *ACS Sens.*, **2024**, *9*, 1, 2-8.
4. A. Nagy, G. Nagy, and Z. Fehér, Investigation of a novel chronopotentiometric detection method using a redox mediator modified carbon electrode, *Anal. Chim. Acta* **1995**, *310*, 2, 241-249.

Single-use Sensor Card for Smartphone-based Home Monitoring of Potassium in Whole Blood

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Close monitoring of the potassium ion concentration in blood is essential for patients suffering from conditions such as chronic heart failure (CHF) or chronic kidney disease (CKD). Maintaining blood K⁺ values in the normal range is essential for these patient groups. The concept aims for a user-friendly self-test performed by the patients themselves at home, comparable to blood sugar self tests for Diabetes patients. [1].

The concept of such an inexpensive and rapid disposable smart test strips comprises a screen-printed electrochemical ISE and reference electrodes, a microfluidic system for sample preparation and delivery, a semiconductor microchip for electrical signal evaluation and a screen-printed antenna for energy harvesting and wireless transmission of the measurement data to a smartphone. Enabling high throughput and low-cost manufacturing will be crucial to allow for successful application of such self- or home testing devices.

We present a polymer-film based sensor-card, comprising a capillary force driven microfluidic system for separation of plasma from whole blood and sequential delivery of sample and calibrator fluid to the screen-printed ion-selective potassium sensor. The fluidic microstructures assist extraction and transport of blood plasma from a porous separation membrane. The microfluidics are directly generated in polymer films by a roll-to-roll extrusion coating technique [2, 3] and is bonded by screen-printed adhesive the sensor sheet carrying printed solid-contact ion-selective electrodes (ISE), antenna structures and the microchip for evaluation and wireless transmission of measurement values.



Figure 1: left: sensor sheet with bonded microfluidics; right: sensor card with smartphone

References:

1. C. Kollegger, P. Greiner, I. Siegl, C. Steffan, M. Wiessflecker, B. Pecec, M. Hajnsek, F. Sinner, G. Holweg, B. Deutschmann. Intelligent NFC potassium measurement strip with hemolysis check in capillary blood, *Elektrotechnik & Informationstechnik*, **2018**, 135, 83–88.
2. P. Tören, M. Smolka, A. Haase, U. Palfinger, D. Nees, S. Ruttloff, L. Kuna, C. Schaudé, S. Jauk, M. Rumpler, B. Hierschlager, I. Katzmayer, M. Sonnleitner, M.W. Thesen, M. Lohse, M. Horn, W. Weigel, M. Strbac, G. Bijelic, S. Hemanth, N. Okulova, J. Kafka, S. Köstler, B. Stadlober, J. Hesse, High-throughput roll-to-roll production of polymer biochips for multiplexed DNA detection in point-of-care diagnostics, *Lab Chip*, **2020**, 20, 4106.
3. S. Murthy, M. Matschuk, Q. Huang, N.K. Mandsberg, N.A. Feidenhans'l, P. Johansen, L. Christensen, H. Pranov, G. Kofod, H.C. Pedersen, O. Hassager, R. Taboryski, Fabrication of nanostructures by roll-to-roll extrusion coating, *Advanced Engineering Materials*, **2016**, 18, 484-489.

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Multiwell Plate-based pH-assay Using Responsive Triangulenium Dyes and ATTO-647

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pH remains the most important chemical parameter and must be monitored for positive outcomes in areas as different as cheese making and diagnostics. Where blood gas analysers enable patient monitoring, starter cultures in cheese manufacturing are still monitored using conventional pH electrodes[1]. Here, we present a multiwell plate format assay for monitoring pH, with the same sensitivity as a pH electrode (≈ 0.05). The assays use a pH responsive triangulenium dye on a polystyrene nanoparticle, and a freely diffusing commercial fluorophore as a reference dye[2]. Experiments were performed in triplicates across three independent sensor component fabrications to investigate and document the performance and robustness of the assay. The pH range, where the assay proved to be operational coincided with the pH range found in in vitro fertilization buffers. Thus, these were used to demonstrate the use of the pH-assay.

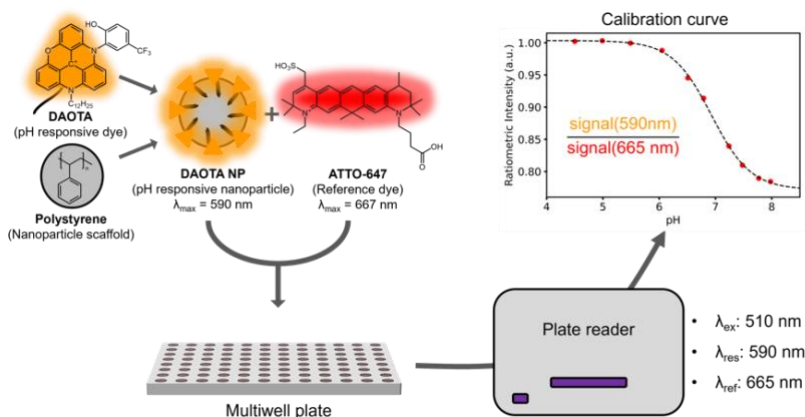


Figure 1. An overview of the pH sensitive nanoparticle formulation and translation into an assay-based platform.

References:

1. B. H. Diehl, M. A. La Pack, T. Y. Wang, R. E. Kottmeier, S. M. Kaneshiro, M. C. Brandenstein, Y. Zhang, Y. C. Chiu, S. Yoon and V. M. Saucedo, *Biopharm Int*, **2015**, 28, 28-31.
2. C. G. Frankær, K. J. Hussain, T. C. Dörge and T. J. Sørensen, *ACS Sensors* **2019**, 4, 26-31.

Enhancing the Binding Avidity of Aptamers for virus Recognition: a Proof of Principle Approach

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Aptamers are small single-stranded artificial oligonucleotides (DNA or RNA) folded into secondary structures and exhibit remarkable binding capabilities to specific epitopes on target molecules [1], even on larger particles, e.g. on viruses [2]. In clinical practice, antibodies are used in protein-based viral assays, but the unique properties of aptamers, including excellent target selectivity, binding affinity and thermal stability, have garnered attention for their potential applications in point-of-need testing. However, in certain cases, e.g. at low target concentration or insufficient affinity, aptamers require further development. To address this, we explored post-selection chemical modifications to enhance their binding avidity. Here we are going to show the proof of principle for virus targets, through the designing aptamer-based multivalent receptors capable of direct virus recognition without causing destruction. Leveraging previously selected [3] and characterized [4] aptamers for the G-protein of Respiratory Syncytial Virus (RSV), we present a proof of principle for this novel approach. This research culminated in the synthesis of a new class of chemically modified aptamers and demonstrating significantly improved avidity for virus recognition. Our findings contribute to the development of new ligands and its potential application on clinical diagnostics and treatments as well.

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References

- [1] A. D. Ellington and J. W. Szostak, "Selection in vitro of single-stranded DNA molecules that fold into specific ligand-binding structures," *Nature* **1992**, vol. 355, no. 6363, pp. 850–852
- [2] E. Torres-Chavolla and E. C. Alocilja, "Aptasensors for detection of microbial and viral pathogens," *Biosensors and Bioelectronics* **2008**, vol. 24, no. 11, pp. 3175–3182
- [3] K. Percze *et al.*, "Aptamers for respiratory syncytial virus detection," *Sci. Rep.* **2017**, vol. 7, pp. 42794
- [4] Z. Szakács, T. Mészáros, M. I. De Jonge, and R. E. Gyurcsányi, "Selective counting and sizing of single virus particles using fluorescent aptamer-based nanoparticle tracking analysis," *Nanoscale* **2018**, vol. 10, no. 29, pp. 13942–13948

Rational Design and Development of Electron Mediators for Enzyme-based Biosensors: Advancing Clinical Diagnostics Through Computational Exploration

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The advancement of clinical diagnostics critically depends on the development of efficient and reliable electron mediators [1,2]. These mediators are pivotal in biosensors, facilitating electron transfer (ET) reactions between the redox-active centers of immobilized enzymes and a conductive electrode support, thus enhancing the sensitivity and selectivity of biosensor devices [2,3].

In this study, we specifically investigate phenazine, quinone, viologen, and their derivatives as innovative electron mediators with promising diagnostic potential. Through meticulous computational predictions, we identify candidates exhibiting not only high solubility and favorable enzyme binding energies, but also appropriate redox potentials conducive to efficient electron transfer processes. Subsequently, these selected candidates undergo rigorous validation processes to assess their performance in clinical diagnostic applications. The results of our experiments demonstrate the effectiveness of these electron mediators in continuous glucose monitoring, blood gas analysis, and test strip platform evaluations.

Guided by the insights gained from computational prediction, our experimental findings unveil promising outcomes, showcasing the potential of these innovative electron mediators to revolutionize clinical diagnostics. This comprehensive approach not only enhances our understanding of electron mediator performance but also paves the way for the development of next-generation biosensor technologies in clinical settings.

References:

1. Katz E., Lioubashevsky O., Willner I., Electromechanics of a redox-active rotaxane in a monolayer assembly on an electrode. *J. Am. Chem. Soc.* **2004**, *126*, 15520–15532.
2. Murphy L. Biosensors and bioelectrochemistry. *Curr. Opin. Chem. Biol.* **2006**, *10*, 177–184.
3. Mohamad Nor N, Ridhuan NS, Abdul Razak K. Progress of Enzymatic and Non-Enzymatic Electrochemical Glucose Biosensor Based on Nanomaterial-Modified Electrode. *Biosensors* **2022**, *12*, 1136.

Polymer Inclusion Membrane-based Separation Method for Milk Sample Pre-treatment Preceding Aptamer-based Sensing

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Aptamers are gaining popularity as biological recognition elements due to their advantages, namely the ease of production and chemical functionalization, high affinity as well as the possibility of counter selection. However, target detection with aptasensors from complex biological samples such as blood, urine or milk is made difficult by the many interfering components. To circumvent loss in performance, sample pre-treatment steps are often employed that are usually lengthy and labor-intensive procedures. In this work, a polymer inclusion membrane (PIM) based sample pre-treatment method is presented, which performs well in the separation and pre-concentration of oxytetracycline (OTC) – a model tetracycline antibiotic – from raw milk samples, prior to detection through aptamer-binding. This is a one-step, easy-to-use method that can even be integrated into flow-through sensing systems.

PIMs have been used for the sample-cleanup of OTC from milk and environmental water samples before HPLC measurement [1,2]. Here, we showcase that this method is also applicable for sample pre-treatment preceding aptamer-based sensing. Circular dichroism (CD) spectroscopy was chosen as the means to confirm aptamer-OTC binding after PIM-based extraction. We have shown earlier that CD is a reliable and simple tool to obtain information on the binding between OTC and its aptamer [3]. The PIM based extraction method was optimized in regards to extraction time, donor and acceptor phase volume ratio and the ionic composition of the acceptor phase.

References:

1. A. Garcia-Rodríguez, V. Matamoros, S.D. Kolev, C. Fontàs, Development of a polymer inclusion membrane (PIM) for the preconcentration of antibiotics in environmental water samples, *J. Memb. Sci.* 492 (2015) 32–39.
2. I. Pérez-Silva, J.A. Rodríguez, M.T. Ramírez-Silva, M.E. Páez-Hernández, Determination of oxytetracycline in milk samples by polymer inclusion membrane separation coupled to high performance liquid chromatography, *Anal. Chim. Acta.* 718 (2012) 42–46.
3. K. Jakab, N. Melios, G. Tsekenis, A. Shaban, V. Horváth, Z. Keresztes, Comparative Analysis of pH and Target-Induced Conformational Changes of an Oxytetracycline Aptamer in Solution Phase and Surface-Immobilized Form, *Biomolecules.* 13 (2023).

DNA Nanocube SAM Scaffolds for FRET-based Biosensing

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DNA SAM based biosensors are proposed to be fast, sensitive, and cost-effective sensors. Control over the monolayer coverage and over the arrangement and spacing between the probes on the surface is required as these have major impacts on the biosensor performance. Using DNA nanostructures is a strategy that can address these issues providing opportunities for rational sensor design. [1,2]

Wireframe DNA nanocube structures[3] were deposited onto a single crystal gold bead electrode surface creating a DNA nanocube self-assembled monolayer (SAM). The DNA nanocubes were specifically adsorbed and oriented using thiol modified DNA on one face of the cube. AFM revealed a uniform coverage with a separation between nanocubes of 20-30 nm. The top face of the cube was designed to allow for interaction with two different complementary DNA strands which contained anchor sequences that specifically hybridize with one edge of the cube, and a linker sequence (30 bases) modified with one of the fluorophores that form a FRET pair (either AlexaFluor488 or AlexaFluor647).[4] The nanocube dimensions controlled the relative spacing between these fluorophores. The FRET signal significantly decreased upon hybridization with the complementary sequence for either linker. Hybridizing the linkers with a biotinylated complementary sequence enabled interaction with Nuetrovidin which was detected through an increase in FRET. The DNA nanocube wireframe was shown to be an effective scaffold for preparing biosensors with a controlled separation between surface-bound probes, enabling a fast equilibrium with targets in solution.

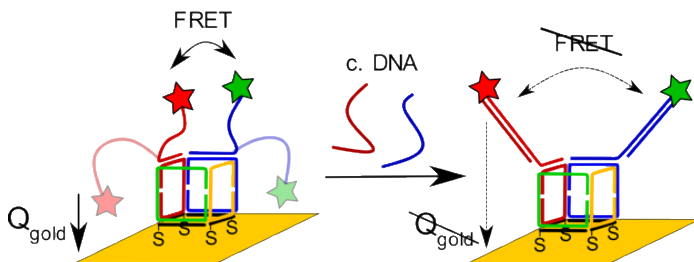


Figure 1: Schematic of DNA nano-cubes deposited on the gold surface via gold-thiol bond, with two FRET compatible fluorophores bound to the top face of the cube; green AF488, and red AF647 before and after hybridizing with complementary strands.

References:

- [1] A. Abi, M. Lin, H. Pei, C. Fan, E.E. Ferapontova, X. Zuo, ACS Appl. Mater. Interfaces 6 (2014) 8928–8931.
- [2] C. Wang, W. Wang, Y. Xu, X. Zhao, S. Li, Q. Qian, X. Mi, Nanomaterials 12 (2022).
- [3] C.M. Platnich, A.A. Hariri, J.F. Rahbani, J.B. Gordon, H.F. Sleiman, G. Cosa, ACS Nano 12 (2018) 12836–12846..
- [4] A.J. Grzedowski, T. Ma, D. Bizzotto, Chemical & Biomedical Imaging 1 (2023) 286–296.

A Generic Approach Based on Long-lifetime Fluorophores for the Assessment of Protein Binding to Polymer Nanoparticles by Fluorescence Anisotropy

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The use of synthetic nanoparticles (NPs) has become indispensable in medical diagnostics, regenerative medicine, drug delivery and in bioassays. When NPs are introduced into living biological systems, a protein layer, the so-called protein corona builds up on their surface, influencing their biological impact and functionality. The protein-NP interactions, either specific or non-specific, are also determinant when using fully synthetic nanoparticle-based affinity reagents for in vitro assays in biofluids.

Here, we put forward a novel general and separation-free approach to quantitate protein-nanoparticle interactions based on measuring the fluorescence anisotropy changes of long-lifetime fluorophore ($\tau >$ several hundred ns) labelled proteins [1]. With conventional fluorophore labels that feature only a few ns fluorescence lifetimes, this is not possible due to the inherently high anisotropy of the labelled proteins that would not change significantly upon binding to a NP. However, with long-lifetime fluorophores, the rotational correlation time of the labelled protein becomes insignificant compared to the fluorescence lifetime and low anisotropy is expected. Binding of the protein to the much larger NPs would result in much higher rotational correlation times, and significantly higher anisotropy values. Thus, the protein-nanoparticle interaction could be sensitively detected and quantified in this way.

As a proof-of-concept, the interaction of lysozyme with engineered NPs was studied by using a long-lifetime, ruthenium complex as label. Fluorescence anisotropy measurements were performed to study the binding kinetics and affinity of the protein to the NPs. The obtained binding isotherm was validated with an independent separation-based method. The bioanalytical use of the proposed approach was also shown through the quantitative assessment of lysozyme by competitive binding to the synthetic NP affinity ligand as a highly relevant model for further molecularly imprinted polymer nanoparticle-based assays.

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References:

1. M. A. Ahmed, D. Hessz, B. Gyarmati, M. Páncsics, N. Kovács, R. E. Gyurcsányi, M. Kubinyi, V. Horváth, *Nanoscale*, **2024**, 16, 3659-67

Novel Electrochemical Sensor Based on Fe Decorated f-MWCNTs Modified CPE for Determination of Estradiol

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Hormones, essential organic compounds in the bloodstream, regulate key biological functions like growth, metabolism, and sexual development. Among female hormones, estradiol (EST) is the most potent estrogen, crucial for various physiological processes within the female reproductive system and beyond. Human and animal excretion releases natural and synthetic hormones into water bodies via sewage and animal waste, raising concerns about their impact on wildlife and humans. Estrogens in surface waters can disrupt sexual cycles and behaviors, compromise immune function, and increase tumor risk [1, 2]. To address this, the European Union proposes monitoring EST levels in surface waters, emphasizing the need for sensitive analytical methods like electroanalysis.

This study introduces the synthesis of functionalized MWCNTs incorporating an immobilized Fe electrocatalyst for the development of a modified carbon paste electrode (Fe/f-MWCNTs-CPE), as a sensor for EST determination. MWCNTs are synthesized using catalytic chemical vapor deposition, followed by functionalization with oxygen-containing groups [3]. Fe/f-MWCNTs are then prepared by immobilizing an iron precursor onto the functionalized MWCNTs and used for sensor fabrication as a bulk modifier of CPE. By using prepared Fe/f-MWCNTs-CPE and utilizing an optimized SWV technique in a phosphate buffer solution at pH 5.0, the sensor can detect EST within a concentration range of 0.25 to 20 $\mu\text{mol/l}$, with a detection limit of 21.5 nmol/l, and direct application to real samples yielding recovery near 100%. Moreover, the sensor demonstrates good selectivity even in the presence of common interfering substances.

References:

1. A. S. Ahmed, The immune system as a potential target for environmental estrogens (endocrine disrupters): A new emerging field. *Toxicology* **2000**, *150*, 191-206.
2. A. M. Andersson, N. E. Skakkebaek, Exposure to exogenous estrogens in food: Possible impact on human development and health. *European Journal of Endocrinology* **1999**, *140*, 477-485.
3. S. Panić, D. Rakić, V. Guzsvány, E. Kiss, G. Bošković, Z. Kónya, Á. Kulkovecz, Optimization of thiamethoxam adsorption parameters using multi-walled carbon nanotubes by means of fractional factorial design. *Chemosphere* **2015**, *141*, 87-93.

MWCNTs Supported Ni and Fe Based Electrocatalysts for Selective Determination of Ibuprofen

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Non-steroidal anti-inflammatory drugs (NSAIDs) play a critical role in managing pain and inflammation, with ibuprofen (IBU) representing a typical NSAID known for its anti-inflammatory, analgesic, and antipyretic properties. Given its extensive usage, the development of sensors for IBU monitoring in various samples, including pharmaceutical formulation and environmental water samples, is crucial for assessing and mitigating the potential environmental and human health impacts of this widely used pharmaceutical compound. Traditional chromatographic techniques necessitate intricate setups and specialized expertise, whereas electroanalytical methods, offer sensitive and selective alternatives. Our study focuses on designing portable, cost-effective sensor platforms like carbon paste electrodes, tailored for highly sensitive IBU detection. With a straightforward synthesis process, a range of MWCNT-based electrocatalysts can be created, serving various applications. Additionally, integrating metals like nickel and iron boosts conductivity and catalytic activity, enhancing the efficacy of these methods.

In this study, we evaluated the performance of carbon paste electrodes (CPE) modified with Ni-MWCNTs and Fe-f-MWCNTs compared to bare CPE. Ni-MWCNTs were synthesized via wet impregnation followed by high-temperature reduction, while Fe-f-MWCNTs were similarly prepared using iron as the modifying agent. Square wave voltammetry was utilized for IBU detection in acetate buffer, revealing LOD and LOQ values of 0.86 and 2.61 μM for bare CPE, 0.13 and 0.39 $\mu\text{mol/L}$ for Ni-MWCNTs-CPE [3], and 0.04 and 0.15 $\mu\text{mol/L}$ for Fe-f-MWCNTs-CPE. These modified sensors demonstrated successful application in pharmaceutical sample analysis, with recovery rates approaching nearly 100%, validating the accuracy and reliability of the modified sensor systems for precise IBU determination. Optimization of the prepared carbon paste-based sensor underscores its potential suitability for routine monitoring of IBU in different real samples.

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References:

1. S. Panić, D. Rakić, V. Guzsvány, E. Kiss, G. Bošković, Z. Kónya, Á. Kulkovecz, Optimization of thiamethoxam adsorption parameters using multi-walled carbon nanotubes by means of fractional factorial design. *Chemosphere* **2015**, *141*, 87-93.
2. A. D. Đurović, V. V. Gudelj, S. Ž. Kravić, S. N. Panić, Z. S. Stojanović, *Monatshefte Fur Chemie* **2024**, <https://doi.org/10.1007/s00706-023-03158-0>.

Poster Abstracts: Thursday

Electrochemical pH Control for On-Site Detection of Lead Traces

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Electrochemical techniques, anodic stripping voltammetry in particular, are suitable to detect trace concentration levels, but only in acidic conditions. However, the pH level of drinking and natural waters is normally varying between 6.5 and 8.5. Therefore, a sensitive detection of lead needs a sample preconditioning to adjust the pH from neutral to acidic conditions. This is most frequently performed by a manual addition of chemicals, such as strong acids.

In this work, an electrochemical method for pH control, involving water electrolysis, is developed to acidify the sample during the sensing of Pb^{2+} traces. An electrochemical cell is designed to integrate two working electrodes: i) a gold screen printed electrode as a sensing electrode and ii) a platinum grid (Pt) as an acidifier. By applying an optimal potential to the acidifier, water is oxidized leading to the electro-generation of protons, which locally reduce the sample pH. The precise control of the pH and the optimization of analytical sensing of lead will be discussed. The developed sensor has a limit of detection lower than the guideline value of 10 ppb (48 nM) of Pb^{2+} in drinking water specified by the WHO [1]. This acidification approach provides an effective lead detection without sample preconditioning, making it particularly suitable for on-site detection applications, and it holds the potential for future detection of other pH dependent analytes.

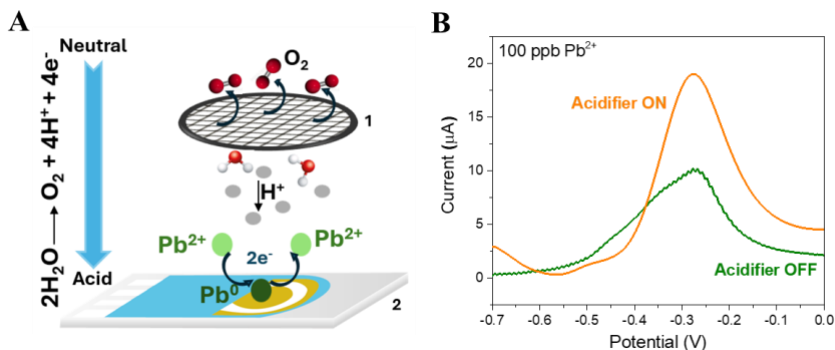


FIGURE (A) Lead detection with in-situ acidification (1) acidifier and (2) sensing electrode (B) Anodic stripping square wave voltammetry of Pb^{2+} with and without in-situ acidification

References:

1. J. Strandberg, Lead in drinking-water, Health risks, monitoring and corrective actions - Technical brief. World Health Organization WHO, 2022 (Available on: <https://www.who.int/publications-detail-redirect/9789240020863>).

Characterisation of Titanium-Oxide Layers for Low-power pH Sensors

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In addition to various biomarkers such as pertinent amino acids, carbohydrates, and antibiotics, pH emerges as another crucial factor for characterizing the metabolic conditions of cell cultures and tissues in Organ-on-Chip setups. Compact and resilient pH sensors have showcased that the sensing characteristics of ion-sensitive metal-oxide (MOx) materials such as RuO₂, IrO₂, TiO₂, SnO₂, Ta₂O₅, WO₃, ZnO, etc. are highly dependent on the stoichiometry, crystalline structure and defects determined by the type and parameters of deposition, or annealing applied [1]. This study focuses on the deposition, structural and chemical analysis, and functional characterisation of varying titanium-oxide layers with different compositions as potential sensitive materials for low-power, pH sensing applications. The titanium-oxide layers were deposited by vacuum sputtering, hydrothermal growing, and atomic layer deposition (ALD) at temperatures of 100°C and 300°C, respectively. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were employed to determine the specific composition and structure of different MOx layers. These MOx-functionalized electrochemical electrodes were connected to the application specific analog front end chip (AFE) of the low-power readout circuit for accurate evaluation. The pH sensitivity of the pH sensing unit, employing various MOx materials, was assessed using pH calibration solutions ranging from pH 8 to 6. Among the other depositions, TiO_x layer deposited via ALD proved more suitable for pH sensing applications, with a slope of 50.2 mV/pH, approximating to Nernstian response.

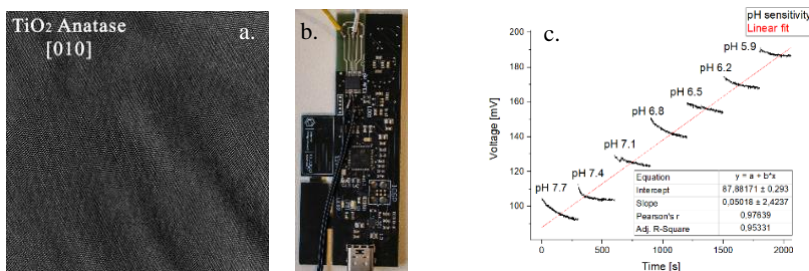


Figure 1. HRTEM image of the high temp. ALD deposited TiO_x layers (a). The manufactured low-power readout circuit (b) and the pH sensitivity of the electrode (c).

References:

1. Bertel, L.; Miranda, D.A.; García-Martín, J.M. Nanostructured Titanium Dioxide Surfaces for Electrochemical Biosensing. *Sensors*, 21, 6167. **2021**.

Nanocomposite-Based Electrochemical Sensors for Biomedical ApplicationsPeng Lei^{a,b}, Shaomin Shuang^b, Yang Liu^a^aCollege of Science and Engineering, James Cook University, Townsville, Australia^bSchool of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, China

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Electrochemical sensors have received considerable interests in the fields of clinical diagnosis and disease treatment due to their advantages of portability, low cost, ease of use, fast response and high sensitivity, making them attractive in the applications where the analysis is expected to shift from central laboratories to the point of care or the point of need, e.g., critical care for people living in rural communities that requires accurate and fast diagnosis.^{1,2} The sensing performance of an electrochemical sensor greatly relies on the material utilized for the working electrode, which converts the information associated with the reaction between an electrode and analyte into an applicable qualitative or quantitative signal. With the rapid development of nanoscience and nanotechnology, nanocomposite materials with tailored structures and synergetic effects have exhibited unique properties for the design of high-performance electrochemical sensors to determine substances of biomedical interest.³ Recently, we have developed several nanostructured composites including Au/Pd-polypyrrole/graphene⁴, CoNi/MOF/graphene⁵ and Cu/Zr MOF nanocomposites⁶, which were employed for electrochemical sensing of DNA bases, glucose and hydrogen peroxide, respectively. In this presentation, the electrocatalytic properties of these nanomaterials, as well as their analytical performance will be demonstrated and discussed.

References:

1. C. Dincer, R. Bruch, E. Costa-Roma, M.T. Fernandez-Abedul, A. Merkoci, A. Manz, G.A. Urban and F. Guder, Disposable sensors in diagnostics, food, and environmental monitoring. *Adv. Mater.* **2019**, *31*, 1806739
2. J. Wang, Electrochemical biosensors: towards point-of-care cancer diagnostics. *Biosens. Bioelectron.* **2006**, *21*, 1887-1892.
3. C. Zhu, G. Yang, H. Li, D. Du and Y. Lin, Electrochemical sensors and biosensors based on nanomaterials and nanostructures. *Anal. Chem.* **2015**, *87*, 230-249.
4. P. Lei, Y. Zhou, B. Li, Y. Liu, C. Dong and S. Shuang, Gold/palladium-polypyrrole/graphene nanocomposites for simultaneous electrochemical detection of DNA bases. *ACS Appl. Nano Mater.* **2022**, *5*, 1635-1643.
5. P. Lei, Y. Zhou, C. Dong, Y. Liu and S. Shuang, CoNi-MOF-graphene magnetic nanocomposites for the electrocatalytic detection of glucose and the efficient removal of organic dyes. *ACS Appl. Nano Mater.* **2023**, *6*, 9369-9375.
6. P. Lei, N. Wu, Y. Zhou, C. Dong, Y. Liu and S. Shuang, Cu/Zr metal-organic frameworks with high peroxidase-like activity for sensitive electrochemical and colorimetric dual-mode detection of hydrogen peroxide released from living cells. *ACS Appl. Nano Mater.* **2024**, *7*, 6556-6563.

Fabricated Microelectrode Sensors for Environmental Monitoring

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In this work we report fabricated ultramicroelectrodes for environmental sensing platform [1]. The three-electrode sensor chip was fabricated in a silicon wafer with 8 working electrodes with HDMI-C connector that can be used for different applications. The microelectrodes have been modified for various application including nitrate in soil, dissolved oxygen, pH sensor, and heavy metal detection. With this platform we can detect the analytes in soil as well in water sources [2]. The nitrate is one of the essential nutrients in soil but because of overuse of fertilizers have made it important to detect the levels of nitrate in soil. A varying nitrate concentration from 1 μM to 100 μM with a sensitivity of 0.038 A/ μM with $R^2 = 0.99$. are investigated using differential pulse voltammetry. The fabricated sensor was also for dissolved oxygen and was studied to monitor the change of dissolved oxygen with the different temperature [3]. The sensor was also tested for heavy metals detection like lead using stripping voltammetry. As lead is linked to several health effects and WHO identifies lead for 143,000 deaths annually the maximum allowable level of lead in drinking water from 50 ppb to 10 ppb. The sensor was modified with different nanomaterials for selective detection of analytes. The final aim of work is developed electronic reader with will allow portable sensing with readout measurement in smart phone application. The fabricated ultramicroelectrodes sensor with these electronics will provide a fully functional system for various environmental monitoring.

References:

1. O’Sullivan, B., O’Sullivan, S., Narayan, T., Shao, H., Patella, B., Seymour, I., Inguanta, R. and O’Riordan, A., 2022. A direct comparison of 2D versus 3D diffusion analysis at nanowire electrodes: A finite element analysis and experimental study. *Electrochimica Acta*, 408, p.139890.
2. Seymour, I., Narayan, T., Creedon, N., Kennedy, K., Murphy, A., Sayers, R., Kennedy, E., O’Connell, I., Rohan, J.F. and O’Riordan, A., 2021. Advanced solid state nano-electrochemical sensors and system for agri 4.0 applications. *Sensors*, 21(9), p.3149.
3. Seymour, I., O’Sullivan, B., Lovera, P., Rohan, J.F. and O’Riordan, A., 2021. Elimination of oxygen interference in the electrochemical detection of monochloramine, using in situ pH control at interdigitated electrodes. *ACS sensors*, 6(3), pp.1030-1038.

Electrochemical and Adsorptive Properties of Laser-treated Boron Doped Diamond Electrodes for Biosensing

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Boron doped diamond (BDD) electrodes possess attractive properties for electrochemical biosensing due to attractive properties including, biocompatibility, low capacitive current, wide potential window and biocompatibility. The sp^3 hybridization of carbon can be converted to sp^2 by laser irradiation with the possibility to accurately control the lateral distribution of sp^2 carbon [1].

This work presents the results on electrochemical characterization of three types of polycrystalline BDD electrodes irradiated by 250 fs 1030 nm IR laser: as-grown undoped diamond electrodes (deposited at B/C in gas phase 0 ppm), as-grown BDD electrodes (B/C ratio 500 ppm) and chem-mechanically polished [2] BDD electrodes (B/C ratio 500, 1000 and 2000 ppm). By laser irradiation sp^2 carbon spots with diameter of 17-35 μ m were formed due to the $sp^3 \rightarrow sp^2$ carbon conversion, covering 0; 0.1; 1; 5; 10; 25; 50, 67% and 100% of surface area. For electrochemical characterization of the BDD electrodes the inner-sphere ($[Fe(CN)_6]^{3-/4-}$) and outer-sphere ($[Ru(NH_3)_6]^{3+/2+}$) redox probes were used. Cyclic voltammetry and electrochemical impedance spectroscopy revealed that the electrochemical parameters (ΔE_p , R_{ct} and Y^0) are greatly affected when sp^2/sp^3 carbon ratio is $\geq 25\%$. Further, increased adsorption of DNA on sp^2 carbon spots was obvious from the fluorescence imaging of SYBR green-labelled DNA. Obviously, laser irradiation opens a way to tailor the electrode surface for specific applications in biosensing.

Acknowledgment:

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References:

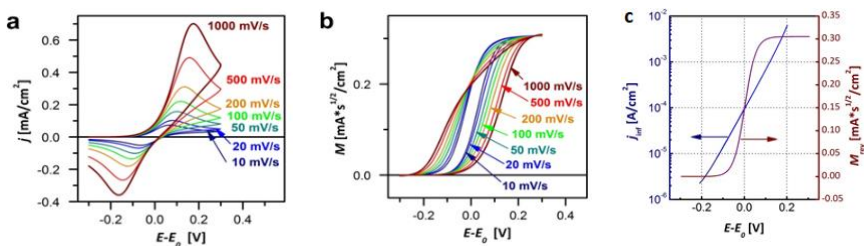
1. J. Hrabovský, M. Zelenský, J. Sladek, M. Zukerstein, J. Fischer, K. Schwarzová-Pecková, A. Taylor, M. Veis, S. Mandal, O.A. Williams, N.M. Bulgakova, Laser-patterned boron-doped diamond electrodes with precise control of sp^2/sp^3 carbon lateral distribution, *Applied Surface Science* **2023**, 639, 158268J.
2. M. Zelenský, J. Fischer, S. Baluchová, L. Fekete, J. Eidenschink, F.-M. Matysik, S. Mandal, O.A. Williams, M. Hromádová, V. Mortet, K. Schwarzová-Pecková, A. Taylor, Chem-mechanical polishing influenced morphology, spectral and electrochemical characteristics of boron doped diamond, *Carbon* **2023**, 203, 363-376.

Analysis of Quasi-reversible CVs and dEIS Data: Transformation to Potential-program Independent Forms

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Dynamic electrochemical impedance spectroscopy, dEIS, comprises repetitive impedance spectrum measurements while slow scan-rate voltammetry is running. Its main virtue is the short measurement time, reducing the danger of contamination of the electrode surface. To further the use of dEIS, we have recently elaborated a set of theories aimed at the related data processing for three groups of fundamental electrode reactions: diffusion-affected charge transfer, charge transfer of surface-bound species, and adsorption–desorption. These theories yielded equations by which the voltammograms can be transformed to potential program invariant forms, allowing an easy calculation of the system parameters like rate coefficients; similar equations have been derived for the potential dependence of equivalent circuit parameters obtained from the impedance spectra. These derivations have also been presented in a single, unified one [1]. An example is shown in the figure below: From a set of “quasi-reversible” CVs taken at varied scan-rates v , two scan-rate independent, hysteresis-free functions can be calculated. One of them is the diffusion-free polarization curve, $j_{\text{inf}}(E)$, the other is the semiintegrated form of the reversible CV, $M_{\text{rev}}(E)$.



Simulated CVs of a diffusion affected charge transfer reaction with varied scan rates (a), their semiintegrals (b), and the calculated j_{inf} and M_{rev} functions (c). Simulation parameters: $D_{\text{red}} = D_{\text{ox}} = 10^{-5} \text{ cm}^2/\text{s}$, $c_{\text{red}} = 10^{-6} \text{ mol}/\text{cm}^3$, $c_{\text{ox}} = 0 \text{ mol}/\text{cm}^3$, $E_0 = 0$, $k_0 = 0.001 \text{ cm}/\text{s}$, $\alpha = 0.5$.

The theory is recommended to evaluate electrode kinetic measurements, particularly when the potential dependence of rate coefficients is under study. Implications to electroanalytical chemistry are also involved.

References:

T. Pajkossy, Determination of Electrode Kinetics Parameters from Dynamic Electrochemical Impedance, Spectroscopy Measurements via Potential-Program Invariant Function, J. Phys. Chem. Lett., **2023**, 14(47), 10599–10608

A Novel Use of Perinone Polymer as an Intermediate Layer: A New Design of Potassium Solid-contact Ion Selective Electrodes.

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Ion-selective electrodes with solid contact (SCISEs) are one of the commonly used potentiometric sensors. For more than 50 years, their design has been improved in order to achieve better and better performing sensors. Eliminating the inner solution resulted in degraded stability and potential reversibility, which in turn negatively affected the reliability and repeatability of measurements. The solution to these disadvantages was the use of a mediation layer, also known as a solid contact. This is such a material, which must have characteristics such as hydrophobicity, chemical stability, mechanical resistance, chemical inertness, and above all, it must present good ion-electron conductivity. There are many materials that show these properties. One of the largest groups of conducting materials are conducting polymers. The most popular organic conductors include polyaniline, poly(3-octylthiophene) and polypyrrole [1,2]. Our research team first used a perinone polymer in the role of a solid contact. These polymers are classified as organic semiconductors due to their properties and consist of monomers that are derivatives of naphthalene and polycyclic aromatic hydrocarbons. Perinone polymers are characterized by a low energy gap, both thermal and electrical stability, high light absorption, very good conductivity, and surprising electroactivity. These polymers include imidazoles and imide groups, giving them even better resistance to high temperatures [3].

Using the new perinone polymer as an intermediate layer, a new type of potassium ion-selective electrodes with solid contact was developed. The perinone polymer layer was applied to the surface of a glassy carbon electrode (GCE) by potentiodynamic polymerization from an electrolyte solution containing polymer monomers. An ion-sensitive membrane was then applied to the properly prepared substrate to provide SCISE with selectivity to potassium ions. In order to check the quality of the prepared electrode, a series of tests were carried out and parameters such as the slope of the characteristic, range of linearity, detection limit, selectivity, reversibility and potential stability were determined, and the effect of the sample environment and measurement conditions on the electrode potential was investigated. In addition, an water layer test was carried out and electrical parameters, i.e. electrical capacitance and resistance, were determined.

References:

1. E. Zdrachek, E. Bakker, Potentiometric sensing, *Analytical Chemistry* **2019**, 91, 2-26
2. C. Wardak, K. Morawska, K. Pietrzak, New Materials Used for the Development of Anion-Selective Electrodes—A Review. *Materials* **2023**, 16, 5779.
3. M. Łapkowski, Perinone – A New Life of an Old Molecule. *Materials* **2021**, 14, 6880.

Unveiling the Kinetic Adsorption and Desorption of Heavy Metals on/off Nanoplastics by Real-time In-situ Potentiometric Sensing

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Nanoplastics ($< 1 \mu\text{m}$) can serve as a transport vector of other environmental pollutants (e.g., heavy metals) and change their toxicities and bioavailabilities [1]. To date, considerable efforts have been devoted to investigate the interactions between heavy metals and microplastics, whereas the behaviors of adsorption and desorption heavy metals on/off nanoplastics are largely unknown. Unfortunately, methodologies associated with the fast and effective separation of the tiny particles (for example, particles smaller than 100 nm) remains a huge challenge. The common methods which are off-site may provide data with long time intervals and even biased information for investigation of heavy metals adsorption and desorption on/off nanoplastics. Potentiometric ion-selective electrodes (ISEs) with attractive features such as fast response, portability and resistance to interference from turbidity, has been a promising tool for in-situ and real-time analysis [2-3]. In this work, the kinetics of heavy metal adsorption and desorption on/off nanoplastics were assessed by using ISEs. Polyvinyl chloride (PVC) and polystyrene (PS) nanoparticles were selected as representative nanoplastics. The influence factors of the interactions between nanoplastics and heavy metals were comprehensively investigated. We found that nanoplastics can adsorb and release heavy metals in a fast manner, demonstrating the superior ability of nanoplastics in transferring heavy metals. The adsorption behaviors are closely related to the characteristics of nanoplastics (e.g., aging treatment, surface groups, particle size and aggregation) and background electrolytes. Particle aggregation and increases in salinity and acidity suppress the adsorption of heavy metal onto nanoplastics. Our proposed method is applicable for detection of the plastic pollutants with size $< 100 \text{ nm}$ and of the samples with high salinities (e.g., seawater). We believe that this work would provide new insights into assessment of environmental risks posed by nanoplastics and heavy metals.

Acknowledgements:

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References:

1. F.H. Song, T.T. Li, J. Hur, F.C. Wu, and X.G. Meng. Eco-colloidal layer of micro/nanoplastics increases complexity and uncertainty of their biotoxicity in aquatic environments. *Environ. Sci. Technol.*, **2022**, 56, 10547-10549.
2. M. Cuartero, N. Pankratova, T. Cherubini, G. A. Crespo, F. Massa, F. Confalonieri, E. Bakker. In situ detection of species relevant to the carbon cycle in seawater with submersible potentiometric probes. *Environ. Sci. Technol. Lett.* **2017**, 4, 410-415.
3. M. P.S. Mousavi, I. L. Gunsolus, C. E. Pérez De Jesús, M. Lancaster, K. Hussein, C. L. Haynes, P. Bühlmann. Dynamic silver speciation as studied with fluoruous-phase ion-selective electrodes: Effect of natural organic matter on the toxicity and speciation of silver. *Sci.Total Environ.* **2015**, 537, 453-461.

Microfluidic Device for Impedance Tomography

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While examining living cells and tissues, priority should be given to avoiding structural damage, and minimizing the influence of external effects. Impedance spectroscopy (EIS) is a widely used method to measure the properties and structure of cells (e.g. size, viability, integrity) in a non-invasive and label-free way, in real time. Impedance tomography (EIST) is one of the most common macroscopic screening methods for body composition measurement and targeted medical diagnostic tests, such as tumor detection [1]. The disadvantage of this technique is that it provides only qualitative, macroscopic information of the tissue, not cellular information. With miniaturization, the cellular resolution would contribute to the in-situ 3D monitoring of the growth of cell cultures, 3D structural changes and the effects of therapeutic treatments [2].

By combining microfluidic systems with EIS, an effective method can be created to support in-depth analysis of site-specific properties of cells and to provide detailed, high-resolution, real-time 3D analysis of their structure, which can be important for drug discovery, personalized medicine, and diagnostics. A layout for EIST was designed and fabricated including 16 equidistant Au or Pt electrodes on glass surface and a microfluidic structure in SU-8 covered by a PDMS top layer for channel formation. The electrode system offers 2- or 4-electrode measurements which can be used to follow the position and adhesion of cells. Feasibility tests were conducted with cell culture media, particle and cell suspensions to monitor position dependent EIS spectra measured in the microfluidic channel.

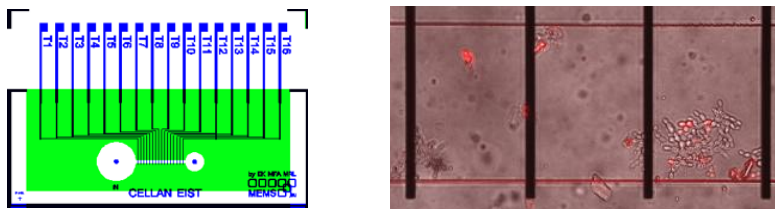


Figure 1. The designed layout for microfluidic EIST measurements (left) and yeast cells inside the microchip (right).

References:

1. D. D. Stupin, E. A. Kuzina, A. A. Abelit, A. K. Emelyanov, D. M. Nikolaev, M. N. Ryazantsev, S. V. Koniakhin, M. V. Dubina, „Bioimpedance spectroscopy: basics and applications,” *ACS Biomaterials Science Engineering*, **2021** 7, 1962–1986
2. M. Schwarz, M. Jendrusch and C. Iordania „Spatially resolved electrical impedance methods for cell and particle characterization,” *ELECTROPHORESIS*, **2019** 41, 65–80

Doped Carbon Thin Films Produced Using Laser-arc PVD Process as a Versatile Electrode Material in Electrochemistry

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The Laser-Arc process is a technique to synthesize hydrogen-free tetrahedral amorphous carbon (ta-C) [1], the hardest type in the family of diamond-like carbon. The advantage of the process is the formation of an ionized, highly energetic carbon plasma, that forms ta-C coatings on almost all substrate materials without any heating. Depending on deposition conditions, the sp^3 -content can be varied up to a maximum of 85 %, but it can also be kept very low to obtain graphite-like amorphous carbon (a-C). The (t)a-C coatings are chemically inert and their electrical conductivity depends on the sp^3 -content and the nanostructure in the coating. Graphite-like a-C-coatings show high potential as thin layers (< 100 nm) on stainless steel bipolar plates of fuel cells due to the unique combination of inertness and electrical conductivity.

The flexible Laser-Arc process allows to dope (t)a-C by nearly any material to adjust its electrical conductivity and surface activity. Doping nitrogen and/or boron, it exhibits semi-conductor behavior with similar electrical properties to boron-doped diamond (BDD) and glassy carbon (GC) electrodes. The determination of the potential window in sulphuric acid shows comparable to higher values compared to the BDD optimized for wastewater treatment of over 4 V. Fundamental redox properties studied with $Fe(CN)_6^{4-/3-}$ and $Ru(NH_3)_6^{+3/+2}$

show optimal reaction kinetics. In addition, these films were applied to non-conductive substrates and electrochemically examined. The properties achieved on glass and plastics are comparable to those on metal substrates.

Furthermore, doped carbon coated electrodes with catalytically active metals were investigated. It was shown that a dopant concentration of approx. 5 at% is sufficient to have a similar behavior as the bulk material of the dopant.

Several other evaluation metrics were used – stability under anodic and cathodic conditions, corrosion resistance, bioanalyte detection, and others.

Overall, this work promotes the development of advanced carbon electrodes for a variety of electrochemical applications. The flexibility of the Laser-Arc coating technology allows almost free adjustment of the coating composition, coating on various substrate materials and scaling up to industrial level with high output.

References:

1. F. Kaulfuss, Materials. **2021**, 14(9)
2. M. Zawischa, Carbon **2023**, 213

Electrochemical Sensor Based on a Lead Film Generated on the Surface of a Multiwall Carbon Nanotubes/spherical Glassy Carbon Electrode for the Determination of Trace Amounts of Europium(III)

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Among electrochemical methods, stripping voltammetry is the most popular, with mercury electrodes being the most commonly used electrodes. The reason for this is that they can be used over a wide range of negative potentials, but also have high polarizability and a smooth surface. Despite these advantages, they have one very important disadvantage, which is the toxicity of mercury. The growing awareness of the toxicity of mercury has prompted the search for alternative electrodes that are friendly to the laboratory environment. Therefore, we proposed to use a carbon nanotubes–based electrochemical sensor for the quantification of europium. Multiwalled carbon nanotubes (MWCNTs) are of great interest due to their unique structural, mechanical and chemical properties. MWCNTs–modified electrodes have excellent electrochemical properties such as wide potential range, low background current, low detection limit, high sensitivity and resistance to contamination [1].

The multiwalled carbon nanotube–based electrodes used enabled a sensitive method for the determination of europium by adsorptive stripping voltammetric (AdSV). The importance of the europium determination method is due to its widespread use in a variety of industries because of its desirable properties. The widespread use of europium(III) results in its continuous release into the environment, which in turn has an impact on living organisms. Europium is a metal that can accumulate in the human body in various tissues, particularly in the bones, and have adverse health effects. Long–term exposure to high levels of europium can lead to adverse health effects such as damage to the kidneys, liver or nervous system. It is therefore necessary to continuously monitor the concentration of this element in the environment, particularly in aquatic ecosystems. In our proposed adsorptive voltammetric procedure for the determination of europium, cupferron, which forms stable and electroactive complexes with europium(III), was chosen as the complexing agent. Lead ions were introduced into the measurement solution to form a lead layer on the multiwall carbon nanotube/spherical glassy carbon electrode, on which the Eu(III)–cupferron complex accumulated, thus increasing the sensitivity of the determination. The developed method was used for the determination of Eu(III)–cupferron in certified reference material and real samples, such as Bystrzyca river water and tap water after enrichment with Eu(III) ions. The obtained results demonstrate the feasibility of using the developed method for the determination of europium in samples with a complex matrix [2].

References:

1. M. Grabarczyk, C. Wardak, R. Piech, A. Wawruch, An electrochemical sensor for the determination of trace concentrations of cadmium, based on spherical glassy carbon and nanotubes. *Materials* **2023**, *16*, 3252.
2. J. Chen, H. Bai, J. Xia, Z. Li, P. Liu, Q. Cao, Q. Electrochemical sensor for detection of europium based on poly–catechol and ion–imprinted sol–gel film modified screen–printed electrode. *Journal of Electroanalytical Chemistry* **2018**, *824*, 32–38.

Direct Printed RVC-based Biocathode for the Construction of Enzymatic Biofuel Cells

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Enzymatic biofuel cells (EBFCs) are a type of electrochemical device that converts chemical energy into electricity. EBFCs are promising power sources for wearable and implantable medical devices. One of the critical points in enzymatic biofuel cell construction is the choice of enzyme immobilization process since it directly affects the lifetime of bioelectrodes [1]. Here, for the first time, we present a direct printed RVC-based working electrode modified with a polyamidoamine (PAMAM) dendrimer and laccase as a biocathode for enzymatic biofuel cell construction. Reticulated vitreous carbon (RVC) is an electrically and thermally conductive porous form of carbon and is characterized by a high surface area [2]. Dendrimers are a class of branched polymers that exhibit highly functionalized terminal surfaces. Due to their organized structure dendrimers have been exploited for enzyme immobilization, in order to increase number of attached biomolecules and their stability [3]. The number of laccases anchored onto linear and dendritic linkers was determined by surface plasmon resonance (SPR). The functionalization procedure with the highest laccase loading was transferred onto RVC-based electrodes, and the electrochemical performance and characteristics of the biocathode were investigated.

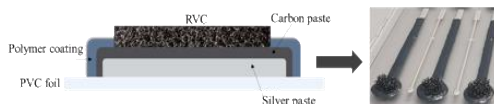


Figure 1. Left: Scheme of the designed RVC-based electrode; Right: photograph of RVC-based electrodes manufactured by a microdosing robot.

References:

1. J. Cai, F. Shen, J. Zhao, X. Xiao, Enzymatic biofuel cell: A potential power source for self-sustained smart textiles. *iScience* **2024**, 27, 1-10.
2. V. M. Vasconcelos, G. O.S. Santos, K. I.B. Eguiluz, G. R. Salazar-Banda, I. Gimenez, Recent advances on modified reticulated vitreous carbon for water and wastewater treatment – A mini-review. *Chemosphere* **2022**, 286, 1-13.
3. M. Urbanowicz, K. Sadowska, B. Lemieszek, A. Paziewska-Nowak, A. Słodatowska, M. Dawgul, D. G. Pijanowska, Effect of dendrimer-based interlayers for enzyme immobilization on a model electrochemical sensing system for glutamate. *Bioelectrochemistry* **2023**, 152, 1-9.

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Utilization of Carbon Nanotubes for Antibody Conjugation in a Sensor for Estradiol Detection

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Estradiol, a key component of the estrogen hormone group, plays a crucial role in reproductive health and the endocrine system. Its presence in water sources has become a significant concern due to its potential impact on aquatic ecosystems and human health[1]. Detecting estradiol in water is essential for several reasons. Elevated levels of estradiol in water can result from the discharge of untreated sewage or agricultural runoff containing hormone-disrupting substances. This can adversely affect aquatic life, disrupting the endocrine systems of fish and other organisms, and leading to reproductive and developmental issues[2]. In this work, we focused on the preparation of a simple immunosensor based on the principle of an antibody bound to the surface of a carbon electrode. During the preparation, we mainly focused on the selection of suitable materials that would serve as a layer for attaching the antibody to the surface of the electrode and would ensure stability and fast signal transmission during the measurement. Carbon nanotubes were chosen as a suitable substance, both multi-walled and single-walled ones were tested in the experiment. The most promising were multi-walled nanotubes, which were then further modified with a carboxyl group or zinc oxide nanoparticles. Carbon nanotubes serve as excellent agents for immobilizing antibodies on the electrode surface in electrochemical sensing due to their high surface area, electrical conductivity, biocompatibility, chemical stability, versatility in functionalization, three-dimensional structure, and enhanced mass transport properties [3]. These characteristics collectively contribute to the development of highly sensitive and reliable electrochemical sensors for various applications, including the detection of specific biomolecules such as hormones or antibodies [4].

References:

1. Nazari, E.; Suja, F., Effects of 17 β -estradiol (E2) on aqueous organisms and its treatment problem: a review. *Reviews on Environmental Health* **2016**, 31 (4), 465-491.
2. Aris, A. Z.; Shamsuddin, A. S.; Praveena, S. M., Occurrence of 17 α -ethynylestradiol (EE2) in the environment and effect on exposed biota: a review. *Environment international* **2014**, 69, 104-119.
3. Tran, T.-T.; Clark, K.; Ma, W.; Mulchandani, A., Detection of a secreted protein biomarker for citrus Huanglongbing using a single-walled carbon nanotubes-based chemiresistive biosensor. *Biosensors and Bioelectronics* **2020**, 147, 111766.
4. Meskher, H.; Mustansar, H. C.; Thakur, A. K.; Sathyamurthy, R.; Lynch, I.; Singh, P.; Han, T. K.; Saidur, R., Recent trends in carbon nanotube (CNT)-based biosensors for the fast and sensitive detection of human viruses: a critical review. *Nanoscale advances* **2023**, 5 (4), 992-1010.

Evaluation of Prussian Blue Deposition methods on carbon-based substrates for use in printed lactate biosensors

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One of the major problems of voltammetric biosensors based on oxidase enzymes is a high overpotential necessary for hydrogen peroxide oxidation (~ 0.7 V vs. Ag/AgCl), whose detection and voltammetric quantification can be used to indirectly determine the quantity of analyte of interest. To avoid interferences due to other substances oxidizing at such high potential, a mediator is used to catalyze either oxidation or reduction of hydrogen peroxide, which reduces overpotential and interference. Due to its high selectivity towards hydrogen peroxide reduction at a low operating potential (~ 0 V vs. Ag/AgCl), Prussian Blue (PB) is a great candidate as a mediator for biosensors detecting analytes such as glucose or lactate [1]. Different deposition methods of Prussian Blue on different carbon substrates (glassy carbon, commercial screen-printed carbon and inkjet printed graphene electrodes) were used and their effect on the properties, stability and functionality of Prussian Blue for detection of hydrogen peroxide was evaluated via cyclic voltammetry. The methods used were chemical deposition [2], electrodeposition [3] and drop casting of synthesized Prussian Blue nanoparticles [4]. Thermal and/or intense pulsed light (IPL) treatment of the inkjet printed electrodes was also performed to yield maximum current responses and minimum peak potential differences of the deposited PB layer. Effect of activation and reaction reversibility of the deposited PB layer was inspected with cyclic voltammetry in 0.1 M KCl from -0.2 to +0.5 V vs. Ag/AgCl with a scan rate 50 mV/s. pH dependent stability of the deposited layer was also inspected via cyclic voltammetry in phosphate buffers (pH 5.4, 6.4 and 7.4). Voltammetric determination of hydrogen peroxide in aqueous media was conducted using the different modified electrodes in batch and flow modes. Finally, a lactate biosensor was assembled by immobilizing lactate oxidase in a chitosan matrix on top of the PB modified electrode and the analytical performance was evaluated.

Acknowledgments:

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References:

1. F. Ricci, D. Moscone, G. Palleschi, Mediated enzyme screen-printed electrode probes for clinical, environmental and food analysis. *Compr. Anal.Chem.* **2007**, *49*, 559-584
2. F. Ricci, A. Amine, G. Palleschi, D. Moscone, Prussian Blue based screen printed biosensors with improved characteristics of long-term lifetime and pH stability. *Biosens. Bioelectron.* **2003**, *18*, 165-174
3. W. Gao, S. Emaminejad, H.Y.Y. Nyein, S. Challa, K. Chen, A. Peck, H.M. Fahad, H. Ota, H. Shiraki, D. Kiriya, D. Lien, G.A. Brooks, R.W. Davis, A. Javey, Fully integrated wearable sensor arrays for multiplexed *in situ* perspiration analysis. *Nature* **2016**, *529*, 509-514
4. S. Cinti, F. Arduini, D. Moscone, G. Palleschi, A. J. Killard, Development of a Hydrogen Peroxide Sensor Based on Screen-Printed Electrodes Modified with Inkjet-Printed Prussian Blue Nanoparticles, *Sensors* **2014**, *14*, 14222-14234

Single Solid-State Ion-Channels as Potentiometric Ion Sensors

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Functionalized nanoporous membranes offer a robust, highly selective alternative to conventional, polymer-based potentiometric membranes [1-2]. These contain an ensemble of surface-modified nanopores, each pore working as an artificial ion-channel. Here, we show that a single solid-state ion-channel can serve as a potentiometric ion sensor, offering tremendous potential for miniaturization. By controlling the surface properties of the nanopores, we could fabricate both cation-permselective, and highly Ag^+ -selective single ion-channels with close-to-Nernstian potential responses to cations. The cation-permselective nanopore was prepared by modifying a single gold nanopore with a thiolated cation-exchanger. The Ag^+ -selective ion-channel was obtained by immobilizing a mixture of three thiol-bearing compounds – an Ag^+ -ionophore, a cation-exchanger, and a hydrophobic alkanethiol – to the inner surface of the gold nanopore.

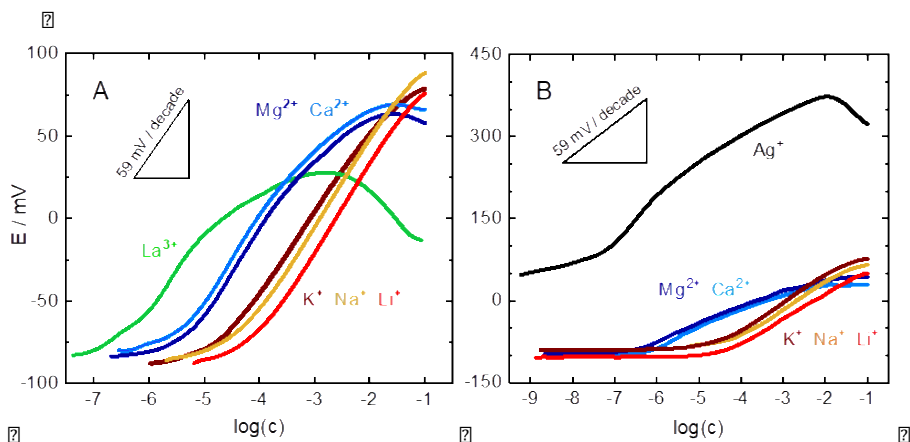


Figure 1. Potential responses of single cation-permselective (A) and Ag^+ -selective (B) 12-nm-radius nanopores recorded with exponential concentration dilution.

References:

1. G. Jággerszki, Á. Takács, I. Bitter, R. E. Gyurcsányi, Solid-State Ion Channels for Potentiometric Sensing. *Angew. Chem. Int. Ed.* **2011**, *50*, 1656-1659.
2. S. Papp, G. Jággerszki, R. E. Gyurcsányi, Ion-Selective Electrodes Based on Hydrophilic Ionophore-Modified Nanopores. *Angew. Chem. Int. Ed.* **2018**, *57*, 4752-4755.