DOI 10.5162/iCCC2026/P7

Ammonium and Potassium Ion-Sensitive Field-Effect Transistors

L. T. Kühne[1], C. Ruffert[2,3], C. Beale[1], M. Wambold[1], E. Kurth[1], O. R. Hild[1]
[1] Fraunhofer Institute for Photonic Microsystems (IPMS), Maria-Reiche-Str. 2, 01109 Dresden, Germany
[2] Fraunhofer Institute for Photonic Microsystems (IPMS), Konrad-Zuse-Str. 1, 03046 Cottbus, Germany
[3] Brandenburgische-Technische Universität Cottbus-Senftenberg
Corresponding author's e-mail address: olaf.hild@ipms.fraunhofer.de

Abstract

The integration of potassium-selective membranes on ion-sensitive field-effect transistors (ISFETs) was successfully reproduced in this study, confirming results previously reported [1]. A sensitivity of 60.2 mV/Dec was achieved in KH_2PO_4/NaH_2PO_4 buffer solution at pH 7, which is in close agreement with the value of 59.3 mV/Dec reported in earlier work. This outcome demonstrates the capacity for stable and reproducible membrane integration, with the potential to approach the theoretical Nernstian response. Furthermore, the coefficient of determination R^2 for all sensors was consistently above 99.75 %, indicating excellent linearity and reliability of the sensor signal. However, measurements performed in a KCl solution buffered with tris(hydroxymethyl)aminomethane to pH 7.6 revealed a significantly reduced sensitivity of 49.36 mV/Dec, despite similar experimental conditions and a still high R^2-value above 99.5 %. This discrepancy suggests a noticeable influence of interfering sodium ions on the sensor's performance, particularly regarding the selectivity of the potassium-sensitive membrane. A comparison of the NH_4^+ sensor reveals a lower sensitivity. The sensitivity is 25.11 mV/Dec and exhibits both a slightly increased variance and a reduced coefficient of determination.

1 Introduction

Ion-sensitive field-effect transistors (ISFETs) are quite promising microdevices for the continuous monitoring of ion activity in biomedical processes. The device's key advantages are its small size, low impedance, and low cost when produced on a large scale. Potassium (K^+) is known to activate numerous enzymatic processes. Consequently, even minor fluctuations in the concentration of K^+ may result in severe ailments, such as arrhythmia and other cardiovascular complications [2-4]. Potassium (K^+) is a vital element for all living cells. In plants it regulates various processes, including growth processes, protein synthesis and stomata regulation, which facilitates gas exchange [5]. Potassium is also of relevance in the field of agriculture, where it plays a crucial role in the synthesis of plant protein and cellulose. In addition, it serves to regulate water balance and control root turgor [6, 7]. The importance of accurate, direct, fast, and cost-efficient K^+-concentration detection capabilities is hence obvious.

Baccar et al. investigated K^+ ISFET microsensors fabricated by ion implantation. The K^+ sensitivity, selectivity, drift, reproducibility, and the lifetime were investigated. The sensitivity of the implanted ISFET equal to 41-44 mV/Dec was still stable after a year's tests with a response range of 10^{-3} to 10^{-1} M [8]. The drift was determined to be smaller than 0.01 mV/h. Two types of sensors were used: **I**) electrolyte-insulator-semiconductor (EIS) structures and **II**) ISFET microsensors using valinomycin as ionophore. The K^+ ISFETs featured an interference for high concentrations of sodium (Na^+) ions.

Benslimane et al. focused on three primary objectives: **I**) to analyse potassium ion levels in Moroccan soils utilizing an ISFET with a selective polyvinyl chloride membrane, **II**) to evaluate the efficacy of different soil-to-water ratios as extraction methods, and **III**) to propose a novel and straightforward extraction technique [9]. The results indicated that the microsensor ISFET provided accurate results on solutions prepared in the laboratory with a correlation factor of 90 % and R² greater than 80 % when estimating potassium levels in soil extracts. The potassium concentration in an aqueous solution was determined by a polyvinyl chloride (PVC) membrane based on valinomycin, tetrakis(4-chlorophenyl)borate as an ionophore, bis(2-ethylhexyl) sebacate (DOS) as a plasticizer, and cyclohexanone as a solvent, using an integrated Ag/AgCl reference electrode. The response range was 5×10^{-4} to 10^{-1} M, and the sensitivity was 48 mV/Dec.

A graphene-based ISFET for potassium sensing was proposed and demonstrated by Fakih et al. [10]. Real-time sensing of K^+ was achieved with a detection limit of 10^{-9} M, and a resolution of $\sim2\times10^{-3}$ log[K^+]. The ISFETs exhibited long-term stability with limited drift over five months. The cross-sensitivity resulted in 2.5 mV/Dec for Na^+, 4.2 mV/Dec for Ca^{2+}, 1.5 mV/Dec for Mg^{2+}, and 9.0 mV/Dec for NH_4^+. Experiments with a variety of specimens confirmed the suitability of graphene ISFETs for K^+ sensing in fluids with multiple solutes.

Riedel et al. [11] found that PVC-membrane ISFETs for K^+, NH_4^+, NO_3^-, and $H_2PO_4^-$ (K^+ and $NH_4^+ \approx$ 50 mV/Dec; $NO_3^- \approx$ 48 mV/Dec; $H_2PO_4^- \approx$ 42 m/Dec) have only a slight long-term drift manifested predominantly as a parallel shift of calibration curves (offset ~0.03 - 0.04 V over three weeks) with unchanged slope.

Hamlaoui et al. [12] reported a zeolite-modified ammonium ISFET using a siloprene membrane incorporating clinop-tilolite. The sensor yielded a sensitivity of ~32 mV/pNH_4^+ and a detection limit of 10^{-8} M. Interferences from H^+, Na^+, and K^+ were negligible (<3 mV/Dec). The device demonstrated stable operation without clinoptilolite leaching for over one month.

In this study, we present a feasibility test of K^+ and NH_4^+ ISFET microsensors as an extension to a previous publication [1].

2 Materials and Method

2.1 Ionophore-ISFET

As a basis for ionophore sensors, we used Ta_2O_5-ISFETs from the 200 mm wafer production line at Fraunhofer IPMS. The p-channel ISFETs were produced on n-type (1-2 Ωcm) 200 mm (100) Si-wafers with dry SiO_2 gate oxide. For the pH-sensitive layer, about 150 nm Ta_2O_5 were deposited onto the gate oxide by r.f. sputtering.

Before coating the ISFETs, they were cleaned with ethanol (15 min) and distilled water. 3 µl of potassium- (with cyclopentanone) or ammonium- (with THF) ionophore cocktail, produced by Aptisens Ltd, were drop-casted and dried for an hour at a maximum temperature of 45 °C. In the drying process, the layer profile becomes inhomogeneous, which means that the layer thickness above the gate may vary. By performing profile measurements, we found that the PVC membrane usually has a crater-like shape, with steep edges and a flatter, more even middle area. Therefore, it was assumed that the diffusion potential is approximately constant over the ISFET channel area.

2.2 Electrical Characterisation

The fabricated ISFETs were operated in constant-voltage, constant-current (CVCC) mode for the measurements. Up to 10 ISFETs could be measured simultaneously in the setup shown in **Figure 1**. The sensors share a common solid-state Ag/AgCl reference electrode, which is mounted into the lid of the measurement chamber. However, for chloride-containing solutions, due to the chloride sensitivity of the solid-state reference electrode, an Ag/AgCl glass reference electrode was used.

The temperature within the measuring vessel was regulated by a thermostat jacket, which was utilized to maintain a constant temperature of 20 °C during the measurements. Using a mechanical stirrer ensured a uniform temperature throughout the electrolyte.

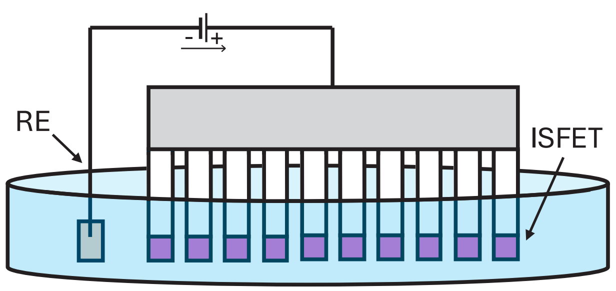

Figure 1 Measurement setup for up to 10 ISFET with a shared reference electrode system (RE).

For all measurements, the drain-source potential (V_{DS}) was set to -0.5 V, the drain-source current (I_{DS}) was set to -200 µA and the bulk-source potential (V_{BS}) was set to 0 V. To characterise the K^+ sensitivity we used **I)** a dilution series of a 1.5 M KCl solution buffered with 0.2 M tris(hydroxymethyl)aminomethane (Tris), adjusted to a pH of 7.6 with HCl and **II)** a dilution series of Merck Certipur® pH 7 buffer, which contains disodium phosphate and potassium dihydrogen phosphate [13]. For the NH_4^+ sensitivity, an ammonium nitrate dilution series was prepared.

The K^+ sensors were conditioned in a 1 mmol/l KNO_3 and NaCl solution, while the NH_4^+ sensors were conditioned in a 0.4 mmol/l NH_4NO_3 solution for a period of 15 hours (overnight) prior to the measurements.

3 Results and Discussion

3.1 Potassium ISFET

First results with Fraunhofer IPMS ISFETs with a K^+-sensitive PVC layer were presented in the first paper [1] with a measured sensitivity of 59.3 ± 0.8 mV/Dec at 20 °C. To confirm this sensitivity and verify a suspected cross-sensitivity, further measurements were conducted in different environments.

In **Figure 2** several ISFETs with a K^+-sensitive layer and one pH-ISFET without a membrane as a reference are presented. The measurement from 1.5 mol/l to 1.5×10^{-4} mmol/l KCl is pH-buffered with tris(hydroxymethyl)aminomethane (Tris) to pH 7.6. The simultaneously measured pH value indicates a deviation at the lowest dilution, due to the very weak buffering effect.

The response of the K^+-sensitive ISFETs in each step is fast but has a slight drift in the dilution. A slight deviation is to be expected, especially in cases of high dilution, as the use of a salt bridge with diaphragm for the reference electrode results in slight contamination with 3 M KCl. However, with uniform contamination, the K^+ slope should only be slightly affected, as each solution has the same amount of additional potassium ions after 30 minutes. Only the actual K^+ concentration used to calculate the linear regression is not precise.

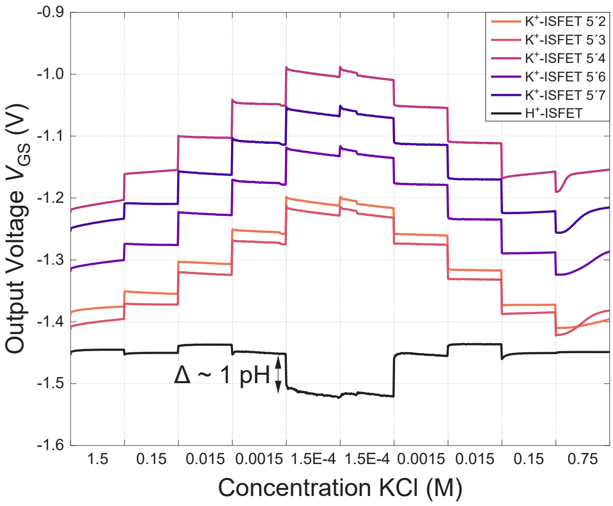

Figure 2 Potassium measurement from 1.5 to 1.5×10^{-4} mol/l KCl, pH-buffered with Tris and with an Ag/AgCl glass reference in 3 M KCl.

The analysis of the voltage values after a settling time of 30 minutes indicates a linear relationship between the sensor voltage and the negative decimal logarithm of the concentration in a range from 0.15 to 1.5×10^{-4} mol/l KCl, as given in **Figure 3**. The concentration range was cropped for evaluation, as the high concentrations fall outside the specifications of the ionophore cocktails.

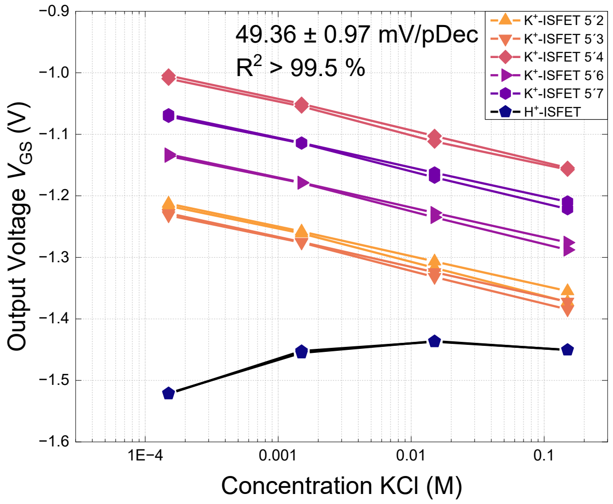

Figure 3 Linear sensitivity to KCl in a concentration range of 150 - 0.15 mmol/l for five representative K^+-selective ISFETs and one pH-ISFET.

The slope of all K^+-sensing ISFET is 49.36 ± 0.97 mV/Dec at 20 °C, in the concentration range from 150 to 0.15 mmol/l KCl. Each K^+ ISFET has a Coefficient of determination R^2 of over 99.5 %.

As already discussed in Sec. 2.1, that the layer thickness of the sensors is expected to exhibit slight inhomogeneity, this represents excellent reproducibility of K^+ sensitivity. The minor variations in sensitivity would be rectified through calibration in later applications, underscoring the significance of achieving a high level of linearity.

For the second potassium measurement, sensitivity was evaluated in a disodium phosphate and potassium dihydrogen phosphate solution. The Merck Certipur® pH 7 buffer was diluted from 1/1 to 1/1000 for this purpose. The fitted slope of 60.20 ± 1.06 mV/Dec for the three K^+-ISFETs (**Figure 4**) is slightly above the Nernstian slope at 20 °C.

These values reproduce prior measurements in KH_2PO_4/NaH_2PO_4 solution, which exhibited a sensitivity of 59.3 ± 0.8 mV/Dec [1] and are consistent with the theoretical Nernst slope for monovalent ions. This outcome demonstrates the capacity for stable and reproducible membrane integration with minimal variation between ISFET sensors apart from baseline offsets. Furthermore, the R^2-value for all sensors was consistently above 99.75 %, indicating excellent linearity and reliability of the sensor signal after calibration.

However, since the measurements performed in a KCl solution buffered with Tris to pH 7.6 revealed a significantly reduced sensitivity of only 49.36 mV/Dec, despite identical test conditions and a still high R^2-value of over 99.5 %, this discrepancy suggests a noticeable influence of interfering Na^+ ions on the performance of the sensor, particularly with regard to the selectivity of the potassium-sensitive membrane. These observed cross-sensitivities are consistent with the results of Riedel et al. [11], who specified a logarithmic selectivity coefficient ($K_{A,B}^{Pot}$) of -3.8 for Na^+ ions for K^+ ionophores.

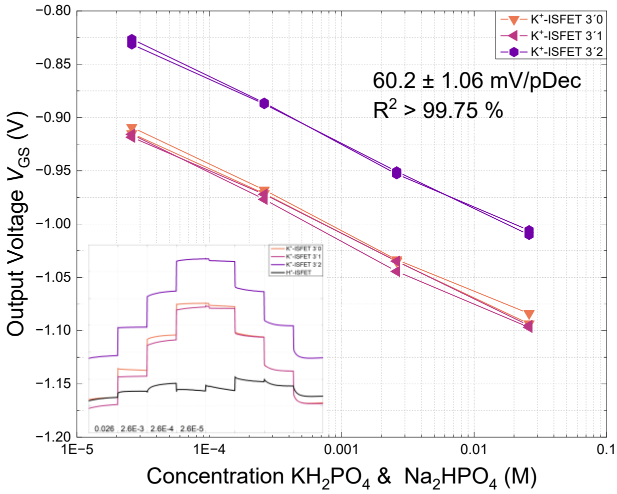

Figure 4 Sensitivity for three K^+-selective ISFETs in a KH_2PO_4/NaH_2PO_4 buffer dilution series at pH 7 measured against a solid-state Ag/AgCl reference.

In conclusion, although the membrane integration is both highly effective and reproducible, the ionic composition of the measurement medium is found to be a crucial factor in determining the sensitivity of the sensor. This highlights the necessity to take cross-sensitivities into account during future calibrations and in application-specific sensor designs.

3.2 Ammonium ISFET

In addition to the successfully integrated K^+ membranes, initial ionophore membranes with ammonium (NH_4^+) were investigated, with a focus on expanding knowledge in the general field of ionophore integration.

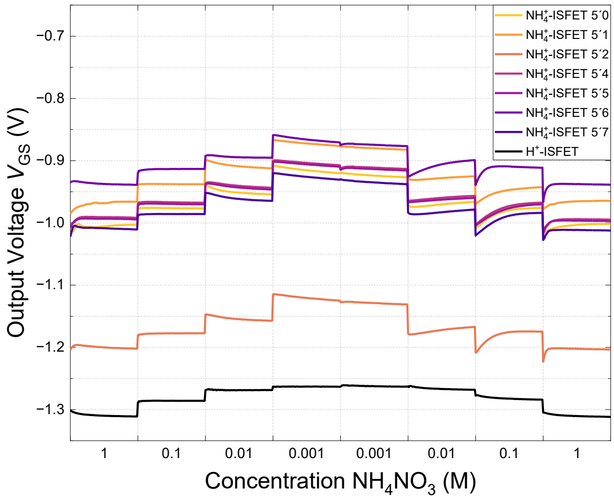

Figure 5 Ammonium measurement from 1 to 1×10^{-3} mol/l of NH_4NO_4, measured against a solid-state Ag/AgCl reference.

Figure 5 provides the measurement curves for seven representative NH_4^+ ISFETs. Additionally, one pH-ISFET is given for reference purposes. In the dilution series, the ammonium nitrate concentration of the solution is first reduced from 1 to 1×10^{-3} mol/l, before gradually increasing back to the initial concentration.

The pH-ISFET demonstrates a slight change in pH value during dilution due to changes in ionic strength and the dissociation equilibrium. These fluctuations have been previously observed in unbuffered solutions and are thus not considered in further discussion. In comparison, the NH_4^+ ISFETs demonstrate a more pronounced increase in output voltage, with clear steps at each dilution stage. A sensor drift is observable in the individual steps, however in contrast to the K^+ ISFET against an Ag/AgCl reference electrode in 3 M KCl, this is not attributable to contamination with the measurement ions or cross ions.

Nevertheless, the slopes in **Figure 6** are 25.11 ± 3.44 mV/Dec, which is only half as steep as that observed in comparable K^+ ISFETs. The R^2-value is found to be acceptable for all NH_4^+ ISFETs at over 96.39 %.

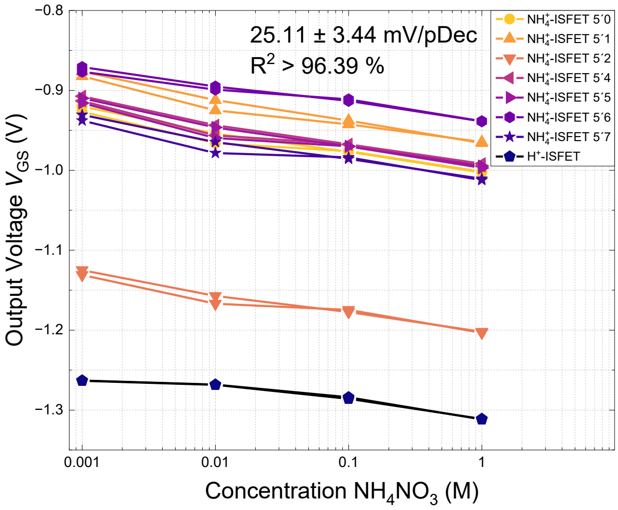

Figure 6 Sensitivity for NH_4^+ selective ISFETs in a NH_4NO_3 dilution series.

4 Conclusion

This work demonstrates the feasibility of integrating K^+ and NH_4^+ selective PVC membranes onto Ta_2O_5-ISFETs, and analyses sensitivity, linearity, and probable cross-sensitivity. Despite the expected inhomogeneity of the membrane thickness, the sensors exhibit strong reproducibility, indicating that the effective diffusion potential across the active gate region remains uniform enough to enable reliable sensing.

Multiple ISFETs with K^+ sensing layers are measured in KCl and KH_2PO_4/NaH_2PO_4 buffer solutions. The slope varied depending on the presence of certain cross ions. A reproducible slope of 59.3 and 60.2 mV/Dec, respectively, was observed in the presence of Na^+ in the dilution series. However, without Na^+ ions, only a slope of 49.36 mV/Dec was observed in a buffered KCl solution. Although different reference electrodes were used for certain reasons, the unmodified ISFETs show that the reference potential does not affect the measurement. This confirms that K^+ ionophores are sensitive to Na^+ ions.

A comparison of the two membranes shows that the NH_4^+ sensitive membranes exhibit a significantly lower sensitivity. The slope is 25.11 mV/Dec and exhibits both a slightly increased variance and a reduced coefficient of determination.

5 Literature

[1] Kühne, L. T., Wambold, M., Beale, C., Al-Falahi, F., Kurth, E., Hild, O. R. u. Ruffert, C.: Ion-Sensitive Field-Effect Transistors for Potassium Sensing. MikroSystemTechnik Kongress 2025. 2025

[2] He, F. J. u. MacGregor, G. A.: Beneficial effects of potassium on human health. Physiologia Plantarum 133 (2008) 4, S. 725–735

[3] Hughes Jr., F. M. u. Cidlowski, J. A.: Potassium is a critical regulator of apoptotic enzymes in vitro and in vivo. Advances in Enzyme Regulation 39 (1999) 1, S. 157–171

[4] Ravens, U. u. Cerbai, E.: Role of potassium currents in cardiac arrhythmias. EP Europace 10 (2008) 10, S. 1133–1137

[5] Leigh, R. A. u. Wyn Jones, R. G.: A hypothesis relating critical potassium concentrations for growth to the distribution and functions of this ion in the plant cell. New Phytologist 97 (1984) 1, S. 1–13

[6] Jackson, D. T. u. Nelson, P. N.: Preparation and properties of some ion selective membranes: A review. Journal of Molecular Structure 1182 (2019), S. 241–259

[7] de Kaiser, Lamb, J. A. u. Rosen, C.: Plant analysis sampling and interpretation University of Minnesota Extension FO-3176-B (2013)

[8] Baccar, Z. M., Jaffrezic-Renault, N., Martelet, C., Jaffrezic, H., Marest, G. u. Plantier, A.: K^+-ISFET type microsensors fabricated by ion implantation. Materials Chemistry and Physics 48 (1997) 1

[9] Benslimane, O., Rabie, R., Diane, A., Bensaleh, M., Saidi, O., Bouzida, I. u. El Hajjaji, S.: Evaluation of Soil Potassium Using Miniaturized Electrochemical Sensors. Ecological Engineering & Environmental Technology 25 (2024) 10, S. 206–215

[10] Fakih, I., Centeno, A., Zurutuza, A., Ghaddab, B., Siaj, M. u. Szkopek, T.: High resolution potassium sensing with large-area graphene field-effect transistors. Sensors and Actuators B: Chemical 291 (2019), S. 89–95

[11] Riedel, V., Hinck, S., Peiter, E. u. Ruckelshausen, A.: Handling of Ion-Selective Field-Effect Transistors (ISFETs) on Automatic Measurements in Agricultural Applications Under Real-Field Conditions. Electronics 13 (2024) 24

[12] Hamlaoui, M., Kherrat, R., Marrakchi, M., Jaffrezic-Renault, N. u. Walcarius, A.: Development of an ammonium ISFET sensor with a polymeric membrane including zeolite. Materials Science and Engineering: C 21 (2002) 1, S. 25–28

[13] Buffer Calibration Standards for pH Measurements MK_BR8716EN, Merck KGaA, 2022