pH-Sensitive Ultra-thin Oxide Liquid Metal System

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Abstract: A complex experiment was performed to unravel the simplest particle, "Higgs Boson," and we performed a simple experiment to address a complex system. We tested the pH response of liquid metal (GaInSn) in the form of a pendant drop and measured the sensitivity of –(92.96±13.54) mV pH⁻¹ in the pH range from 4 to 10. We derived a unified Nernst equation to explain high pH sensitivity and coincidentally rediscovered Marcel Pourbaix's illuminating work on the ‘pH-Potential Diagram.’ The surface potential in the sensor probe is originated from a spontaneous electrochemical reaction purely driven by thermodynamics, rendering to the lowest system energy possible. Our findings have a great scientific significance, which could redefine the conventional concept of the ion sensing mechanism in a solid-state electrochemical sensor.

Keywords: Hydrogen ion, pH, pH Sensor, ISFET, EGFET, 2D material, liquid metal, 2D oxide, Nernstian Sensitivity, Pourbaix pH-Potential Diagram
I. Introduction
Richard Feynman's famous quote, "There is plenty of room at the bottom," initiated the dawn of nanotechnology back in 1959, and the world sees the tremendous progress of technological advances in many areas of modern science. Discovery of graphene (Novoselov, Geim et al. 2004)\(^1\) from natural graphite in 2004 resonate the world's scientific community and creates a sustainable research opportunity in 2D materials with an immense possibility. Atomically smooth 2D natural superficial oxide on liquid Gallium and its alloys is recently isolated in 2017 (Zavabeti, Ou et al. 2017)\(^2\), which expands the horizon of 2D material.

Gallium and its eutectic alloys EGa\(_{0.685}\)In\(_{0.215}\)Sn\(_{0.10}\) (Galinstan) are liquid metal near or below room temperature, offering unique material properties including high electrical and thermal conductivity, excellent fluidity and flexibility, non-toxicity and biocompatibility. An ultra-thin oxide (0.5~3 nm) formation (Regan, Tostmann et al. 1997)\(^3\) on liquid metal with ambient air or trace-amount of oxygen (<1 ppm) gives the liquid metal an added attribute, which enables its application much more appealing to the scientific community (Dickey 2014, Mukhopadhyay, Karuppannan et al. 2020)\(^4,5\). In recent times, liquid metal research gets substantial momentum with several noteworthy findings (Chen, Liu et al. 2018, Yu, Chen et al. 2018, Mukhopadhyay, Karuppannan et al. 2020)\(^5,7\), which has widened the scope of future research (Chen, Wang et al. 2020)\(^8\). With the growing interest of soft, flexible, and wearable sensors, a liquid metal-based sensor is proven to be effective in biomedical areas (Tang, Cheng et al. 2018)\(^9\) including health monitoring, electronic skin, strain sensor, temperature (Ota, Chen et al. 2014)\(^10\) and humidity...
sensor (Ota, Chen et al. 2014)\textsuperscript{10}, and also an electrochemical sensor for detection of heavy metals ions (Sivan, Tang et al. 2013)\textsuperscript{11}, gases (Han, Yang et al. 2019)\textsuperscript{12}.

Among various electrochemical sensing, pH sensing is particularly essential as pH level influences most of the reactions in analytical chemistry, biology, and environmental science. The metal-metal oxide system is a well-known material for solid-state pH sensors (Głab, Hulanicki et al. 1989)\textsuperscript{13}. Naturally, the idea comes to explore the potential of liquid metal featuring superficial oxide as a pH sensor. E. Mitraka et al.(Mitraka, Kergoat et al. 2015)\textsuperscript{14} investigated screen printed hybrid electrode comprised of GaInSn embedded in a conducting polymer (PEDOT) matrix for pH threshold indicator. It utilizes the amphoteric properties of gallium oxide in low pH (pH=2) to activate the electron transfer between GaInSn and PEDOT. To test the merit of liquid metal Ga-Ga\textsubscript{2}O\textsubscript{3} system as a pH sensor, we systematically investigated the pH sensing properties of liquid metal in the form of a pendant drop (\textbf{Fig. 1A}) using MOSFET (metal-oxide-semiconductor field-effect transistor) as a transducer. The ion-sensitive FET (ISFET) was first introduced by Bergveld in 1970 (Bergveld 1970)\textsuperscript{15} and become mainstream of sensor technology for detecting pH and many different ions, DNA, and biomolecules. The ISFET was further evolved to a simpler version (van der spiegel, Lauks et al. 1983)\textsuperscript{16} as extended gate FET(EGFET), which dramatically reduce the effort of complex fabrication of ISFET. In EGFET, the gate of the main FET is connected by a signal line to a low impedance ion-sensitive membrane, which only interacts with the analyte during testing. We extensively studied the pH sensing performance of liquid metal, especially the sensitivity and linearity, through a series of electrical measurements and analysis in the pH buffer range of 4 to 10. (\textbf{Fig. 1B and Fig. 1C})

\textbf{II. Results}
Open Circuit Potential (OCP) Measurement

Without any transducer (MOSFET), one can easily estimate the intrinsic surface potential induced in a metal-metal oxide sensor electrode referenced with an Ag-AgCl electrode by measuring OCP (Chung, Sulkin et al. 2014). OCP reflects the true potential of a spontaneous electrochemical reaction at or near thermodynamics equilibrium. We tested nine fresh liquid metal GaInSn drops for OCP measurement in the pH buffer from 4 to 10 and recorded the corresponding stable voltage reading from a precision multimeter. We plotted the measured OCPs vs. pH variations with an error bar to estimate the average sensitivity and linearity of the liquid metal sensor probe. (Fig. 1D). The average sensitivity and linearity are – (94.17±13.54) mV pH⁻¹ and R²=0.9922±0.0047, N=9, respectively.

EGFET LMPD (Linear Region of MOSFET Operation)

The basic MOSFET theory is fully applicable to ISFET or EGFET with a slight modification of threshold voltage term by including the electrochemical cell potential (E_{ECP}), which is induced as a surface potential in the sensor probe. In electrochemistry, an electric potential is usually denoted by E instead of V. The E_{ECP} or only E is the electrode potential which is described satisfactorily by the Nernst equation:

$$E_{ECP} = E^0 - \frac{RT}{n_e F} \log(a_{H^+}) = E^0 - \frac{RT}{n_e F} pH$$

(1)

E₀ is the standard cell potential, R is the universal gas constant, T is the absolute temperature in Kelvin, F is the Faraday constant, nₑ is the number of electron transfer in the process, and a_{H⁺} is
the activity of hydrogen ion in the solution. After one step of calculation (see SM) by putting the 
values of all the parameters, it becomes the familiar Nernst equation,

\[ E = E^0 - \frac{0.0591}{n_e} \log(a_{H^+}) = E^0 - \frac{0.0591}{n_e} \rho H \]  

(2)

The EGFET operated in the linear region \((V_{DS} < V_{GS} - V_{th\text{ (MOSFET)}})\) the drain current \((I_{DS})\) is 
expressed as:

\[ I_{DS} = \mu_n C_{ox} \frac{W}{L} V_{DS} \left[ V_{\text{REF}} - (V_{th\text{ (MOSFET)}} \pm E_{ECP}) - \frac{1}{2} V_{DS} \right] \]  

(3)

where \(\mu_n C_{ox}(W/L)\) is the intrinsic parameter of MOSFET, \(V_{\text{REF}}\) is the reference bias voltage, 
\(V_{th\text{ (MOSFET)}}\) is the threshold voltage of MOSFET without any influence of \(E_{ECP}\), and \(V_{DS}\) is the 
drain-source voltage. We measured the transfer characteristics of EGFET (GaInSn LMPD) in the 
linear region for various pH buffer from 4 to 10 and plotted the curves, as shown in Fig 2A. The 
curve shifts in a linear fashion with increasing (decreasing) of pH \((H^+\text{ ion})\) values of the buffer 
solution (pH 4 to 10). We tested fifteen fresh liquid metal EGaInSn drops in EGFET 
configuration. We extracted the \(V_{\text{REF}}\) data at100 \(\mu A\) from each LMPD’s transfer characteristic 
and plotted \(V_{\text{REF}}\) vs. pH values with an error bar (Fig. 2B) to estimate the average sensitivity and 
linearity. The average sensitivity and linearity are \(- (92.96\pm13.54) \text{ mV pH}^{-1}\) and 
\(R^2=0.9898\pm0.0122\), respectively. We also tested pure Gallium liquid metal drop for further 
confirmation. We measured the transfer characteristics and estimated the sensitivity similar to the 
GaInSn probe. The sensitivity and linearity for a typical Ga LMPD are \(-110.78 \text{ mV pH}^{-1}\) and 
\(R^2=0.9953\), respectively. (Fig. 2C, Fig. 2D). We fabricated a read-out circuit based on similar 
EGFET to monitor the real-time sensor output voltage with the variation of the pH buffer.
solution. The average sensitivity and linearity of EGaInSn-LMPD obtained from the read-out circuit are – (97.01±8.10) mV pH⁻¹ and R²=0.9940±0.0048, N=12, respectively (see SM).

III. Discussion

Quest for the Origin of High Sensitivity in LMPD

We see in the literature that the sensitivity of a pH sensor is usually related to Nernst potential of -59.1 mV pH⁻¹, which has a good analogy of the sub-threshold swing (SS) of 60 mV dec⁻¹ of the semi-classical field-effect transistor. The sensitivity of more than -59.1 mV pH⁻¹ measured from pH sensor is often explained with ambiguity. We wonder how a transducer (MOSFET) with SS of 60 mV dec⁻¹ can be probed to detect ionic activity more than the conventional limit (-59.1 mV pH⁻¹) even the latter was derived(Yates, Levine et al. 1974)¹⁸ from the same Boltzmann distribution considering energy among classical (distinguishable) particles. The present understanding of the underlying mechanism of chemical sensing in the solid-state sensor has been carried forward from the beginning of its inception in 1970(Bergveld 1970)¹⁵ to until now(Manjakkal, Dervin et al. 2020)¹⁹. We experienced clear signals from sensors on many occasions to uncover the truth but ignore unconsciously because of the dominance of the existing site binding model (Yates, Levine et al. 1974)¹⁸, complemented with many experimental results. We rather start to interpret our high value of sensitivity as an exception of classical Nernst equation involving more than one hydrogen ion per one-electron transfer in the process of sensing. Liquid metal in the form of pendant drop gives pH sensitivity as low as -71 mV pH⁻¹ to as high as -110 mV pH⁻¹. It is indeed exciting to obtain high sensitivity in the new wonder material after graphene, but seeking for the true origin of sensitivity gave us sleepless nights.
Look Back as Far as Possible

Modern electrochemistry always will be indebted to Josiah Willard Gibbs and Walther Nernst, the two finest electrochemist worlds have ever seen. In the late 19th century, J.W. Gibbs formulated a theory to predict whether a chemical reaction would be spontaneous based on the free energy concept popularly known as Gibbs free energy expressed below,

$$\Delta G = \Delta G^0 + RT \times \ln Q$$  \hspace{1cm} (4)

Here, $\Delta G$ the change in Gibbs free energy, $T$ is the absolute temperature, $R$ is the gas constant, $Q$ is the reaction quotient.

In the 20th century, W. Nernst extended Gibbs' theory to include the contribution from the electric potential of charged species. The change in Gibbs' free energy of an electrochemical cell can be related to the cell potential ($\Delta G = -nFE$, $\Delta G^0 = -nFE^0$). Therefore, Gibbs' theory in Nernst representation will be written as follows:

$$n_eF \Delta E = n_eF \Delta E^0 - RT \times \ln Q$$  \hspace{1cm} (5)

Here, the $n_e$ is the number of electrons, $F$ is the Faraday constant, and $\Delta E$, $\Delta E^0$ are the cell potential under non-standard and standard condition (T= 298K, P= 1 atm, and M=1 mole), respectively. By dividing the amount of charge transferred ($n_eF$), Nernst arrived at a new equation. Finally, the Nernst equation is:

$$\Delta E = \Delta E^0 - \frac{RT}{n_eF} \times \ln Q$$  \hspace{1cm} (6)
In a galvanic cell, where a spontaneous redox reaction drives the cell to produce an electric potential, the change in Gibbs free energy must be negative. In a galvanic electrochemical cell, it is always a redox reaction that can be broken down into two half-cell reactions: oxidation occurs at the anode, where there is a loss of electrons, and reduction occurs at the cathode, where there is a gain of electrons. Electricity is generated due to the electric potential differences between the two electrodes (lumenlearning.com)\textsuperscript{20}. The Nernst equation can be used to calculate the output voltage changes in a pair of half-cells under non-standard conditions.

**Electrochemical Cell and Potentiometric Sensor**

Potentiometric sensors measure the potential difference between two electrodes under the condition of no current flow. These sensors are often called an electrochemical cell as the working principle is fundamentally inherited from the previous one. In a potentiometric sensor, two half-cell reactions take place at each electrode. Only one of the reactions should involve sensing the species of interest. The other should be a well understood reversible and non-interfering reaction occurring in the Ag-AgCl reference electrode.

**Metal-Metal Oxide pH Sensor**

Usually, metal-metal oxide electrodes respond to pH buffer solution through a reversible electrochemical reaction (Głab, Hulanicki et al. 1989)\textsuperscript{13}. Ideally, the metal does not take part in the potential determining reaction. We will clarify this statement later.

The redox reaction occurring at the electrode-electrolyte interface can be expressed as follows:

\[
M_xO_y + 2yH^+ + 2ye^- \leftrightarrow xM + yH_2O
\]  

(7)
The electrode potential can be calculated for the above reaction as follows,

\[
E = E^0 - \frac{0.0591}{2y} \log[a_{H^+}^{2y}] - \frac{2y}{2y} \times 0.0591 \log[a_{H^+}]
\] (8)

Therefore, the sensitivity will be -59.1 mV pH⁻¹ at 298 K. The possible redox reactions for Ga-Ga₂O₃ system can be written as follows,

\[Ga_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Ga + 3H_2O\] (9)

An intermediate oxide Ga₂O can be formed during the reaction, but it is less stable and readily transfer to metallic Ga. These reactions are as follows,

\[Ga_2O_3 + 4H^+ + 4e^- \leftrightarrow Ga_2O + 2H_2O\] (10)
\[Ga_2O + 2H^+ + 2e^- \leftrightarrow 2Ga + H_2O\] (11)

As an equal number of ions \((n_{H^+}/n_{e^-})\) exchange occurs during the process, naturally, the sensitivity will be -59.1 mV pH⁻¹.

Different equilibrium reactions other than three (eq. 9, 10, and 11) mentioned above only could initiate sensitivity more than -59.1 mV pH⁻¹. We could establish a general equation from our intuition with asymmetric ion exchange in the interface without knowing much about the specific reactants and products. We could express a redox reaction involving asymmetric ion exchange as follows:

\[mA + n_{H^+}H^+ + n_{e^-}e^- \leftrightarrow nB + cH_2O\] (12)

The electrode potential equation for the above reaction is given below:


\[ E = E^0 - \frac{0.0591}{n_e} \log \left( \frac{(a_B)^n (a_{H,O})^c}{(a_A)^m (a_{H^+})^{n_{H^+}}} \right) = E^0 - 0.0591 \left( \frac{n_{H^+}}{n_e} \right) \log(a_{H^+}) - \frac{0.0591}{n_e} \log \left( \frac{(a_B)^n (a_{H,O})^c}{(a_A)^m} \right) \]  

(13)

Assuming the activity of A, B, and H2O to unity, the equation could be simply expressed as follows,

\[ E = E^0 - 0.0591 \left( \frac{n_{H^+}}{n_e} \right) \log(a_{H^+}) = E^0 - 0.0591 \times x \times \log(a_{H^+}) \]  

(14)

The ion exchange factor ‘x = n_{H^+}/n_e’ will determine the exact electrochemical cell potential, which will be induced as surface potential (sensitivity) in the sensor probe during spontaneous electrochemical reaction with the analyte.

We walked far from the initial experimental results of pH sensitivity in our liquid metal probe. Let us recall the values for the ease of relating it with the just derived generalized Nernst equation for pH sensitivity. The average sensitivity is -92.96 mV pH\(^{-1}\) for EGaInSn-LMPD and -110.78 mV pH\(^{-1}\) for Gallium-LMPD. The value of ‘x’ is close to 1.57 for EGaInSn and 1.87 for Gallium.

Deep knowledge of thermodynamics and electrochemistry is required to establish a chemical reaction involving asymmetric ion-exchange factor to corroborate high pH sensitivity values in our system. The second phase of the sleepless night started for the search of any existing chemical reactions if available for Gallium in pH solutions. To our great surprise, within a few days of rigorous search, we found a research article (Dickey 2014)\(^4\) of liquid metal referring Pourbaix diagram for explaining chemical interaction of liquid metal (Ga or EGaInSn) in acidic and basic environments.
Pourbaix’s ‘pH-Potential’ Prediction and relation to the Ga-Ga₂O₃ System

In no time, we found a book entitled “Atlas of Electrochemical Equilibria in Aqueous Solutions” (Pourbaix 1974)²¹, which is based on Marcel Pourbaix’s doctorate thesis in 1945 at the Technical University of Delft. In the book’s foreword, W. G. Burgers described that “the introduction into electrochemistry of potential-pH diagram in the form originated byPourbaix marks a new era in the study of electrochemical reaction occurring in an aqueous medium near an electrode.” Based on the fundamental foundation of thermodynamics and electrochemistry, it is possible to predict for a given element, the equilibrium states of all the possible reactions between the element, its ion and its solid and gaseous compound in the presence of water(Pourbaix 1974)²¹.

We found the following reactions of Gallium, as stated below,

\[
\begin{align*}
Ga + 2H_2O & \leftrightarrow GaO_2^- + 4H^+ + 3e^- & (15) \\
Ga + 3H_2O & \leftrightarrow HGaO_3^{2-} + 5H^+ + 3e^- & (16) \\
Ga + 3H_2O & \leftrightarrow GaO_3^{3+} + 6H^+ + 3e^- & (17)
\end{align*}
\]

For these reactions, electrode potential can be written as follows.

\[
E = E^0 - 0.05916 \left( \frac{4}{3} \right) \log(H^+) - 0.0197 \log(GaO_2^-) 
\]

(18)

Similarly, the electrode potential for reaction stated in eq. 16 and 17 as follows,

\[
E = E^0 - 0.05916 \left( \frac{5}{3} \right) \log(H^+) - 0.0197 \log(HGaO_3^{2-}) 
\]

(19)
The pH sensitivity calculated from these three equations is -78.8 mV pH$^{-1}$, -98.5 mV pH$^{-1}$, and -118.2 mV pH$^{-1}$, respectively. The values are close to our measured pH sensitivity. The average sensitivity of EGaInSn and Gallium are -92.96 mV pH$^{-1}$ and -110.78 mV pH$^{-1}$, respectively. The values are approaching the theoretical maximum values of -98.6 mV pH$^{-1}$ and -118.2 mV pH$^{-1}$ for the Ga-Ga$_2$O$_3$ system. The gallium-based anions \( \text{(GaO}^-, \text{HGaO}^-, \text{and GaO}^{3-}) \) are simply behaving as counter-ion and will not contribute to the overall pH response. One may easily confuse with series of possible reactions for a given material and its oxides. It can be easily understood from the basic principle of thermodynamics and Gibbs's free energy concept. Depends on materials, the interfacial reaction automatically selects the reaction to minimize the system energy. For example, in our Ga-Ga$_2$O$_3$ system, the common reactions with symmetric ion exchange in the interface (\( n_{H^+}/n_{e^-}=6/6=1 \)) or (\( n_{H^+}/n_{e^-}=3/3=1 \)) will result in a sensitivity of -59.1 mV pH$^{-1}$. The change of oxidation number of materials involves in the redox reaction purely controls the number of electron transfer in the interface during sensing. As the system will always render to minimize the energy, the next possible reaction occurs at \( x=4/3=1.33 \), resulting in a sensitivity of -78.8 mV pH$^{-1}$. Similarly, we may get a sensitivity of -98.5 mV pH$^{-1}$ and -118.2 mV pH$^{-1}$ for higher-order ion exchange (\( x=5/3, 6/3 \)) at the interface depending on the sensing material purity.

The purity of EGaInSn and Ga used for the experiment is 99.99% (4N), and 99.999% (5N) (see SM), and we noticed at least 10 mV pH$^{-1}$ sensitivity differences between two LMPD probes.

Here we would like to understand the nature of ‘\( x \)’. The \( n_{H^+} \) is the number of hydrogen ion adsorbed in the sensor surface, and its values are 1, 2, 3, ..., \( n \). The \( n_{e^-} \) is the change of oxidation

\[
E = E^0 - 0.05916 \left( \frac{6}{3} \right) \log(H^+) - 0.0197 \log(GaO_{3}^{3-})
\]
number of the material involved in the reactions. Therefore, ‘x’ has a precise stepwise discrete value, which in turn control sensitivity in a similar discrete manner.

Although the sensitivity is approaching to the theoretically predicted value; the differences arise between the theoretical and experimental sensitivities owing to the deviation of material electronic configuration from its ideal one. The ideal electronic configuration of the material may perturb owing to strain, impurity, defects, and scattering, etc. Here we propose and introduce an entirely new parameter, Pourbaix factor ‘pb’ (in the honor M. Pourbaix’s work), which quantitively represents the deviation of materials quality from its ideal monolayer form. The experimental sensitivity reported in the literature may have a certain degree of measurement error. For simplicity, we may include measurement error in sensitivity values into our Pourbaix factor (pb). The new Nernst equation by including Pourbaix factor (pb) can be written as follows,

\[
E = E^0 - 0.0591 \times pb \times x \times \log(a_n) \]

The value of ‘pb’ will be between 0 and 1 (0 < pb < 1).

Validation of Pourbaix factor in Gallium Nitride (GaN)-Ga2O3 system

In the case of a gallium nitride system, the native oxide is also Ga2O3. One can wonder why such system never exhibits sensitivity more than -59.1 mV pH⁻¹? The system is already perturbed by the incorporation of nitrogen (N) into Gallium (Ga), which leads to imperfection in native Ga2O3. We estimated the Pourbaix factor for the GaN-Ga2O3 system based on the lattice parameters of Ga (Barrett and Spooner 1965) and GaN (Leszczynski, Teisseyre et al. 1996). The Pourbaix factor (pb) can be calculated from the expression stated below,
As we said, the system will always try to minimize its energy, the next possible reaction after \( x=3/3 \) (-59.1) for \( \text{Ga}_2\text{O}_3 \) will be for \( x=4/3 \) ( -78.8 mV pH\(^{-1} \)). Due to imperfection in \( \text{Ga}_2\text{O}_3 \), the actual sensitivity will be -78.8 \times 0.7046=-55.60 \text{ mV pH}\(^{-1} \) (considering lattice constant \( a \)) and -53.41 mV pH\(^{-1} \) (considering lattice constant \( c \)). M. Bayer et al. (Bayer, Uhl et al. 2005) calculated sensitivity of -55.90 mV pH\(^{-1} \) using density functional theory (DFT) without any influence of site binding model, which is similar to the sensitivity which, we just derived considering Pourbaix factor.

Based on experimental and theoretically predicted pH sensitivities, we introduce a compact sensitivity (\( S \)) vs. Pourbaix-ion exchange (pbx) factor plot to represent all the possible sensitivity values for Ga-Ga\(_2\)O\(_3\) system (Fig. 3A). The origin (0,0) simply denotes the reference electrode potential as we always measure the potential of the working electrode (sensor probe) referenced to the Ag-AgCl electrode. For simplicity, we set the reference electrode potential as zero. The family of line with decreasing slope represents the sensitivity with different Pourbaix factor (pb).

Critical Discussion

Nernstian sensitivity is estimated by assuming one-electron exchange through the interface. However, it is the ion exchange factor \( x=1 \), which determines the sensitivity of -59.1 mV pH\(^{-1} \).

Depending on the value of \( x \), the sensitivity will evolve from sub-Nernstian (\( S< -59.1 \)) to Nernstian (\( S\sim-59.1 \)) to super-Nernstian (\( S> -59.1 \)) regime. We propose to simply assign it
as ideal Pourbaix sensitivity as the occurrence of lower and higher-order (except the ideal one, x=1) ion exchange in the interface was originally predicted by M. Pourbaix.

One may wonder why such high sensitivity is not usually accessible for thick metal-metal oxide or metal-oxide sensing film. For thick oxide, the higher-order ion exchange reactions are not likely possible as the sensing film’s resultant electronic configuration largely deviates from its ideal monolayer’s electronic configuration. The natural oxide with a high degree of perfection only can exhibit a higher order of ion exchange in the interface during electrochemical reactions, which is mostly missing in the case of thick oxide grown on the arbitrary substrate.

In the case of quasi 2D or 2D oxide nano-film, the resultant electronic configurations, energy levels, chemical bonding, and hence the interfacial interactions with the analyte, are approaching the ideal theoretical standard of the elemental oxide itself. The limitation caused by the structural features of bulk material are alleviated in 2D film, and the intrinsic material properties are overwhelmingly effective by the resulting properties in the 2D structure. On EGaInSn (Gallium) energetically favorable self-limiting, amorphous (poorly crystalline) Ga$_2$O$_3$ is formed in the metal-air interface, which is atomically thin and extraordinarily smooth naturally grown 2D oxide(Regan, Tostmann et al. 1997, Zavabeti, Ou et al. 2017)$^{2-3}$. Moreover, the Ga$_2$O$_3$ is relieved from the strong covalent bonding in an orthorhombic crystal structure upon its formation from liquid Gallium, and the weak van der Waals (vdW) force only exists between oxide and metallic core. Therefore, the higher-order ion exchange is very susceptible to the EGaInSn-Ga$_2$O$_3$ system, which leads to high sensitivities.
We should clarify the role of bulk GaInSn or Gallium in the pH sensing process as we repetitively mention metal-metal oxide system on many occasions. We know that the spontaneous redox reaction is an entirely interfacial phenomenon that is driven towards establishing an equilibrium involving Ga and its oxide or oxide ions. More specifically, equations 9, 15, 16, and 17 represent the way the system gradually tends to minimize its energy. Metal does not take part in a potential determining reaction as the oxidation state of the metal is unaltered and remains at 0 (M⁰) in the whole ion sensing process. Metal electrodes are used purely for signal transmission from sensor probe to transducer and provide a stable foundation to grow respective oxides (Pd-PdO, Ir-IrOx, Ru-RuOx) for ion sensing. The OCP and EGFET configuration allows low impedance metal-metal oxide (M-MₓOᵧ) membrane as a sensing probe. In contrast, ISFET allows both low and high impedance (Ta₂O₅) metal oxide (MₓOᵧ) film as a sensing membrane.

IV. Validation through Graphene, Ir-IrOx, and Pd-PdO (GrIP) System

We would like to emphasize that our newly introduced Pourbaix ion-exchange factor (pbx) could explain and unify all the pH sensitivities data scattered around the literature unequivocally. "Extraordinary Claims Require Extraordinary Evidence " (ECREE), a famous phrase was made popular by astronomer Carl Sagan. This aphorism is at the heart of the scientific skepticism, model for critical and rational thinking. We attempted to validate our claim by systematic analysis and explanation of reported sensitivities values of several materials system extensively used for pH sensing to get a good grip on the topic.
Graphene

Graphene has been extensively studied as an enhanced sensing membrane for chemical and biological species (Zhang, Jing et al. 2020)\textsuperscript{25}. The origin of the large variation in reported pH sensitivity ranging from as low as -6 mV pH\textsuperscript{-1} (Fu, Nef et al. 2011)\textsuperscript{26} to as high as -98 mV pH\textsuperscript{-1} (Ang, Chen et al. 2008)\textsuperscript{27} remains unclear. One can relate the variation of pH sensitivity to the quality of graphene as it varies among different laboratories based on the synthesis, isolation, and transfer techniques. Graphene quality is indeed compromised with the use of polymer (PMMA) in device processing steps and not fully recovered even after the most crucial cleaning through annealing (Lin, Lu et al. 2012)\textsuperscript{28} steps. In an attempt to unravel the origin of pH sensitivity, Fu et al. (Fu, Nef et al. 2011)\textsuperscript{26} concluded that graphene being saturated bond of carbon atom is, in fact, insensitive to pH variation in a solution. It irks us to think how a chemically inert materials’ Dirac point (charge neutrality point) is so sensitive to charge puddle (Samaddar, Yudhistira et al. 2016)\textsuperscript{29} at or near the graphene surface. The use of graphite and graphene as active anode material in Lithium-ion battery (Raccichini, Varzi et al. 2015)\textsuperscript{30} contradicts its insensitivity towards H\textsuperscript{+} ion. Based on Pourbaix’s prediction, ideal graphite (C) could exhibit pH sensitivity of -59.1 (x=2/2, 4/4), -73.9 (x=5/4), and -88.6 (x=6/4) mV pH\textsuperscript{-1} (see SM). The possible lower-order ion-exchange reaction (x=1/4, 2/4) would give the sensitivity of -14.79 and -29.58, which are few milli-volts (mV) above the experimentally observed sensitivity by I. Heller et al. (Heller, Chatoor et al. 2010)\textsuperscript{31} and Y. Ohno et al. (Ohno, Maehashi et al. 2009)\textsuperscript{32}, respectively. The higher order ion exchange factor x=7/4 could result in -103.53 mV pH\textsuperscript{-1}, which is close to the value of -98 mV pH\textsuperscript{-1} (Ang, Chen et al. 2008)\textsuperscript{27}. Pourbaix factor pb=0.203 and 0.271 together with ion exchange factor (x=2/4) could explain the extracted sensitivity of -6 mV
pH\textsuperscript{-1} and -8 mV pH\textsuperscript{-1} for chemical vapour deposited (CVD) and exfoliated graphene, respectively (Fu, Nef et al. 2011\textsuperscript{26}). The pH response of graphene through a sensitivity vs. compact pbx plot is shown in Fig. 3B.

**Ir-IrOx**

Ir-IrOx system is one of the most attractive electrodes for pH sensing. Extensive research results on Ir-IrOx system were elucidated by Glab et al. (Glab, Hulanicki et al. 1989\textsuperscript{13}, Peter et al. (Kurzweil 2009)\textsuperscript{33}, and M. Khalil et al. (Khalil, Liu et al. 2018)\textsuperscript{34}. Depending on the preparation method of Ir-IrOx film, two trends from reported sensitivity are prominent. IrOx film deposited by thermal evaporation and sputtering technique resulted in maximum sensitivity of -59 mV pH\textsuperscript{-1}. In contrast, the electro-deposited (anodic oxidation) of IrOx film resulted in high sensitivities from -69.9 to -90 mV pH\textsuperscript{-1} (Burke, Mulcahy et al. 1984\textsuperscript{35}). With an exception, S. Chakraborty et al. (Chakrabarti, Maikap et al. 2017)\textsuperscript{36} reported that the sputtered deposited 2 nm IrOx film, sensitivity reached to -115 mV pH\textsuperscript{-1}. However, for 5 nm IrOx film, the sensitivity again dropped to -50 mV pH\textsuperscript{-1}. Based on Pourbaix’s prediction, Ir-IrOx could exhibit pH sensitivity of -59.1 (x=6/6, 4/4, 2/2), -98.5 (x=10/6), and -118.2 (x=4/2) mV pH\textsuperscript{-1}(see SM). The Ir-IrOx film prepared by the physical vapor deposition method is usually anhydrous, whereas anodic oxidation will always result in hydrated Ir-IrOx film. The degree of hydration in the sensing film plays a vital role during the actual sensing process and enhances the sensitivity to a higher value than -59.1 mV pH\textsuperscript{-1}. On the contrary, S. Chakraborty et al. (Chakrabarti, Maikap et al. 2017)\textsuperscript{36} actually created a quasi 2D ultra-thin IrOx film by precisely controlling deposition thickness to 2 nm in the sputtering technique. The dense nano-pore in the film resulted in a discrete island-like structure, which reduces the overall carrier scattering. Therefore, it is
reasonable to obtain the high sensitivity of -115 mV pH\(^{-1}\), which is approaching the theoretically predicted value of -118.2 mV pH\(^{-1}\) (x=4/2). All those experimental sensitivities could be accommodated in the S-pbx plot considering the change of oxidation number (1, 3, 4, 6) in the redox process, as shown in Fig. 3 (C).

**Pd-PdO**

It is well-known that Pd and PdO readily adsorb hydrogen gas at room temperature. Based on this unique property of palladium, Pd-PdO system has been studied for potential pH sensor applications. Several preparation routes had been used in earlier studies to form a uniform PdO coating on Pd metal. Chemical oxidation of Pd metal in high temperature or reactive sputtering of PdO produced coating of polycrystalline PdO, which exhibited sensitivity close to -59 mV pH\(^{-1}\)(Grubb and King 1980)\(^{37}\). C.C. Liu et al.(Liu, Bocchicchio et al. 1980)\(^{38}\) used electrochemical anodic oxidation for miniaturized Pd-PdO wire electrode, which showed a high sensitivity of – (71 ± 5) mV pH\(^{-1}\). A low-temperature solution process with optimized annealing of Pd-PdO film resulted in a relatively high sensitivity of -64.71 mV pH\(^{-1}\)(Qin, Alam et al. 2016)\(^{39}\). A Pd-PdO coated electrospun fiber for wearable sensors recently is reported by V. C. Diculescu et al.(Diculescu, Beregoi et al. 2019)\(^{40}\). The reported sensitivity varies from -28 to -59 mV pH\(^{-1}\). Based on Pourbaix’s prediction, Pd-PdO could only exhibit pH sensitivity of -59.1 (x=2/2, 4/4) (see SM). We could use different ion exchange factors for explaining the experimental sensitivities in Pd-PdO system. A compact plot of S-pbx for Pd-PdO system is presented in Fig. 3D. (continued-See SM)

**V. Conclusion**
Ever-increasing research in recent times on liquid metal in the field of flexible and wearable sensors motivated us to study the pH sensing properties of liquid EGaInSn-Ga$_2$O$_3$ systems systematically. The high sensitivity in the liquid metal system is originated from the higher-order ion-exchange ($x>1$) occurring in the ultra-thin oxide-pH buffer interface. The whole ion sensing process is a spontaneous interfacial electrochemical reaction well described by Gibbs, Nernst, and Pourbaix equations. We found that Nernstian sensitivity of -59.1 mV pH$^{-1}$ occurs only for symmetric ion exchange ($x=1$) reactions. Asymmetric ion exchanges could result in sensitivity far beyond the Nernst sensitivity, depending on the properties of the material. We derived and validated a generalized equation by including ion exchange ($x$) and Pourbaix factor ($pb$) in the well-known Nernst equation, which could explain almost all sensitives values available in the literature. High sensitivity (> -59.1 mV pH$^{-1}$) is usually inaccessible in the thicker oxide owing to the intrinsic material and electronic properties. However, in a quasi 2D or 2D oxide, the electronic interaction is approaching the elemental monolayer oxide level resulting in an enhanced interaction in the interface; hence the high sensitivity is easily attainable. Our study on the liquid metal system paves the way for developing next-generation electrochemical sensors based on 2D oxides. It will indeed be fascinating to exploit the potential of Gallium based liquid metal as a reaction medium to grow natural 2D oxides other than Ga$_2$O$_3$ for potential electrochemical sensor applications.

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**Supplementary Materials:**
Materials and Methods
Supplementary Text
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References (S41-S55)
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**Fig. 1. LMPD’s pH sensing characterization** (A) Photograph of liquid metal pendant drop (LMPD). The liquid metal drop is hanging from the narrow aperture of the stainless needle. The superficial thin oxide gives suitable mechanical stability to the drop and perfectly balances the downward gravitational force, which prevents pendant-drop from dropping immediately. (B) Schematic diagram to visualize the liquid metal drop in the pH buffer environment. The oxide layer is immune in pH range from 4 to 10. Liquid metal comprised of an inner liquid metal core and an ultra-thin natural surface oxide Ga\(_2\)O\(_3\) (0.5~3 nm). (C) Schematic representation of potentiometric measurement setup of LMPD vs. Ag-AgCl electrode using (i) open circuit potential (OCP) (ii) extended gate (EG) FET and (iii) FET based constant voltage constant current read-out interface circuit (CVCC-ROIC) techniques. (D) Measurement result from OCP of nine LMPDs in different pH buffer solutions. The pH sensitivity and linearity were extracted through a linear fit of measured data points.
Fig. 2. Electrical characterization of LMPD (A) Transfer characteristics of EGFET GaInSn LMPD in different pH buffer solutions from 10 to 4. The LMPD probe responds well with pH change as the curve is gradually shifting towards the right with increasing pH value (decreasing H+ ion concentration). (B) Fifteen GaInSn LMPD probes’ VREF at IDS=100 µA with corresponding pH values plotted with error bar for estimation of average sensitivity and linearity. (C) Transfer characteristics of EGFET Ga LMPD in different pH buffer solutions from 10 to 4. (D) For a typical Ga LMPD, VREF vs. pH plot for the sensitivity and linearity calculation.
Fig. 3. Sensitivity vs. compact Pourbaix and ion exchange factor (S-pbx) plot for Ga-Ga$_2$O$_3$ and other material systems. (A) Sensitivity vs. ion exchange factor (Pourbaix factor) plot to visualize all possible sensitivity values which could be obtained through different pbx factors. Based on our experimental highest sensitivity in the Ga-Ga$_2$O$_3$ system, the pbx is set to 2 to accommodate all the sensitivity values. S vs. pbx plot for (B) Graphene (C) Ir-IrOx and (D) Pd-PdO system. Available experimental sensitivities from the literature are plotted in terms of the Pourbaix factor (pb), which give a sense of deviation of the material quality from the ideal one.
|     | a(Å)  | c(Å)  | \( p^b_e \) | Sensitivity (mV pH\(^{-1}\)) | \( p^b_c \) | Sensitivity (mV pH\(^{-1}\)) | Sensitivity (mV pH\(^{-1}\)) |
|-----|-------|-------|-------------|-----------------------------|-------------|-----------------------------|-----------------------------|
| Ga  | 4.5258| 7.6570| 0.7046      | \(-78.9 \times 0.70\) = -55.60 | 0.6773      | \(-78.9 \times 0.67\) = -53.41 | -55.90                      |
| GaN | 3.1890| 5.1864|             |                             |             |                             |                             |

**Table 1. Pourbaix factor in GaN-Ga\(_2\)O\(_3\) system:** Parameters for calculation of ‘pb’ in GaN-Ga\(_2\)O\(_3\) system and associated pH sensitivity
Supplementary Materials for
pH-Sensitive Ultra-thin Oxide Liquid Metal System

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This PDF file includes:

- Materials and Methods
- Supplementary Text
- Figs. S1 to S9
- Tables S1
- Captions for Movies S1 to S3

Other Supplementary Materials for this manuscript include the following:

- Details calculation of Nernst potential and sub-threshold swing (SS) of MOSFET
- Certificate of Analysis (COA) of GaInSn (4N) and Ga (5N) provided by RICH-Metals, Inc., China

References: S41-S55
Materials

Eutectic Gallium alloy EGaInSn (Galinstan) and Gallium (Ga) with of purity 99.99%(4N) and 99.999% (5N) were purchased from RICH-METALS Inc, China. NIST standard different pH buffer solutions of pH 4, 6, 7, 8, 10 were purchased from Alfa Aesar Inc and Hanna Instruments Inc. A double junction Ag-AgCl (OHAUS STREF1) reference electrode was purchased from Analytical Instruments, Inc, China. An n-type enhancement mode MOSFET in a commercial IC CD4007UBE (Texas Instrument CD4007UBE: CMOS dual complimentary power plus inverter) was used as the electronic transducer for EGFET configuration and characterizations.

Methods

Liquid Metal (GaInSn and Gallium) Sensor Probe Setup

We filled liquid EGaInSn in a 1 mL syringe fitted with a stainless-steel dispensing needle with a diameter of 0.6 mm. The liquid metal in the syringe would come out from the pinhead aperture of the needle with a gentle push of the syringe’s piston. Careful control of the piston movement would form a drop of liquid metal suspended from the pinhead aperture, which we call ‘Liquid Metal Pendant Drop’ (LMPD). The hanging electrode concept was adapted from a polarography experiment date back in 1954 by P. A. Giguère et al. (Giguère and Lamontagne 1954)41. We also prepared Gallium LMPD for the pH response measurement. Initially, Gallium was melted in a temperature bath maintained at 35°C, and we filled some molten liquid gallium in a syringe (same preparation as EGaInSn LMPD). The molten liquid Gallium still maintains its liquid state even the temperature is lower than 29.76°C (melting temperature of Ga), because of the...
supercooling effect. We soldered a wire on the stainless needle towards the syringe side, which provided the electrical contact between the LMPD probe and the MOSFET gate.

Electrical Measurement of LMPD Sensor (OCP and EGFET)

We measured open circuit potential (OCP) between the LMPD probe referenced to an Ag-AgCl electrode by a precision digital multimeter (Hewlett Packard HP E2378A). We built an electrical measurement system in a NI-PXIe-1073 chassis with an integrated controller. We installed NI PXI-4132 programmable high-precision source measurement units (SMUs) and a NI-PXIe 6361 DAQ in the NI-PXIe-1073 chassis. A Keithly 2400 low voltage source meter was used as another SMU as two SMUs are required to characterize the three-terminal device i.e., MOSFET(EGFET). We developed a LabVIEW Programming interface to control both the SMUs and DAQ. Complete measurement setup, materials, components, measurement instruments are presented in Fig. S1-S3. The schematic diagram for the I-V measurement of LMPD EGFET is illustrated in Fig. S4. Transfer characteristics of n-MOSFET without LMPD and gate leakage characteristics (with and without LMPD) are shown in Fig. S5A-B. We performed all the electrical characterization of both EGaInSn and Ga LMPD pH sensor at room temperature (298K) and ambient conditions.

Constant Voltage Constant Current (CVCC) Read-Out Interfacing Circuit (ROIC)

The CVCC-ROIC plays a crucial role in miniaturization and easy integration of ISFET and EGFET devices for monitoring the ionic concentration in target analyte in real-time. A conventional floating source type CVCC was first introduced by Caras and Janata (Caras and
Janata 1980) in 1980 to measure the differential drain current of ISFET(ENFET). The read-out circuit designed for ISFET and EGFET is the simplest way to get the sensor output signal without the use of expensive semiconductor parameter analyzer or multiple source-measurement units (SMU). A suitable CVCC-ROIC for ISFET or EGFET (Kaisti, Boeva et al. 2016) turns the stable sensor probe to a portable sensing device.

We developed a CVCC-ROIC in this study to measure the LMPD sensor output voltage with different pH buffer solutions. A schematic circuit diagram of CVCC ROIC is illustrated in Fig. S6. The primary function of the CVCC ROIC presented here is to measure sensor output voltage ($V_{OUT}$) with the variation of pH of the buffer solution, which senses $E_{ECP}$ in the LMPD probe attached to the MOSFET gate. The MOSFET should operate in the linear region ($V_{DS} < V_{GS} - V_{th}$) and should be biased at constant voltage and constant current (CVCC) mode to monitor the change of ionic (H$^{+}$ ion for pH) activity in the analyte. These conditions make the gate-source ($V_{GS}$) voltage proportional to the internal threshold voltage ($V_{th}$) of the MOSFET.

The drain current of EGFET in the linear region (equation 3 in the main manuscript) is rearranged as follow:

$$I_{DS} = \mu_n C_{ox} \frac{W}{L} V_{DS} \left[ V_{LG} - (V_{th(MOSFET)} \pm E_{ECP}) - \frac{1}{2} V_{DS} \right]$$

The reference bias ($V_{REF}$) applied to the analyte can be broken down into at least two parts. $V_{LL}$ is the voltage drop in the analyte, and $V_{LG}$ is the voltage applied to the LMPD probe. However, $E_{ECP}$ is induced during the sensing process, which contributes to the overall voltage at LMPD. If $V_{REF}$ is kept constant, then induced $E_{ECP}$ will be reflected in the actual gate-source terminal as
$V_{GS}$. The equation 24-25 represent the above statement through a few mathematical formulations.

\[
V_{REF} = V_{LL} + V_{LG} \tag{24}
\]

\[
V_{LG} = f(V_{REF}, E_{ECP}) \tag{25}
\]

\[
V_{GS} = f(V_{LG}) = f(E_{ECP}) \tag{26}
\]

By replacing $V_{LG}$ to $V_{GS}$, equation 23 is rearranged to visualize the purpose of CVCC as follows,

\[
V_{GS} = \frac{I_{DS} W}{\mu_c C_{ox} L V_{DS}} + V_{th(MOSFET)} \pm E_{ECP} + \frac{1}{2} V_{DS} \tag{27}
\]

The $V_{GS}$ of MOSFET is proportional to the $E_{ECP}$ when other parameters ($I_{DS}$ and $V_{DS}$) on the right-hand side are kept constants. We assembled CVCC ROIC on custom made PCB platform. The circuit is comprised of OP-AMPs (Kaisti, Boeva et al. 2016)\(^{43}\) (LTC 6079 Linear-Quad CMOS Input/output amplifiers), current source & current sink (Texas Instrument REF200-Dual 100 $\mu$A current source/sink), passive components (resistor), and DC voltage source. In our CVCC ROIC, the MOSFET was biased at $I_{DS}=100\, \mu\text{A}$ and $V_{DS}=0.5\text{V}$, respectively, so that it could operate in the linear region. The two OP-AMPs acts as a voltage follower with unity gain so that the output voltage is equal to the input voltage. Current source ($I_{Source}$), OP-AMP 1, and resistor $R_V$ keeps the drain-source voltage ($V_{DS}$) constant at 0.5V, which is possible because OP-AMPs have very high input impedance and ideally draws no current. Thus, $R_V$ keeps $V_{DS}$ constant together with $I_{Source}$. The current sink ($I_{Sink}$) ensures a constant current of 100 $\mu$A flowing through the drain to the source terminal. Any variation of pH in analyte sensed as $E_{ECP}$ in the LMPD probe will modulate gate potential ($V_{GS}$). Since the gate voltage is grounded ($V_G=0$) through a reference electrode (Ag-AgCl), any change in $V_{GS}$ will change $V_S$ and finally reflected...
in $V_{OUT}$ through OP-AMP 2. We verified the linearity of CVCC-ROIC by a sweeping DC voltage signal ($V_{IN}$) fed directly to the n-MOSFET gate through SMU-2, and the output signal $V_{OUT}$ was measured through one of the input channels of DAQ. We found a linear correlation (Fig. S7A) between $V_{OUT}$ and $V_{IN}$, as expressed below.

$$V_{OUT} = 0.6514V_{IN} - 0.6764, R^2 = 0.99$$ (28)

The output voltage obtained from CVCC ROIC ranges from 600-1300 mV with good linearity, which was suitable to measure the output-voltage for pH range 10 to 4. We measured the output voltage of the LMPD probe using an analog input port of DAQ in real-time with a fixed $V_{REF}$ of 3V. The $V_{REF}$ was set in such a way that it should be equal or higher than the $V_{REF}$ value for pH10 at 100µA (See Fig. 2A). During the measurement of EGaInSn LMPD, we captured a screenshot of $V_{OUT}$ vs. time trace, which is shown in Fig. S7B. For a typical LMPD, the measured output voltage with time is measured and plotted, as shown in Fig. S8A. We found that the output voltage ranges from 650 mV to 1100 mV for the pH ranges of 10 to 4. The sensitivity extracted from the read-out circuit will be low because of the correlation between $V_{OUT}$ and $V_{IN}$ (equation 28). A simple conversion is required to get correct sensitivity of the LMPD probe from read-out circuit which is expressed below,

$$S_{LMPD} = \frac{S_{CVCC}}{0.651}$$ (29)

where $S$ represents sensitivity. Twelve fresh LMPD sensors were tested in CVCC-ROIC setup, and $V_{OUT}$ vs. pH with error bar is plotted in Fig. S8B. The average sensitivity and linearity of the LMPD sensor are - (97.23±8.10) mV pH$^{-1}$ and 0.9938±0.0048, respectively. The sensitivity and
linearity of the LMPD sensor obtained from both EGFET and read-out circuits are similar in magnitude.

**Supplementary Text**

(This is the continuation of the main manuscript. We presented an additional analysis and discussion on the experimental value of sensitivity for different materials systems available in the published literature to strengthen our claim.)

**Ru-RuOx**

RuOx is a conducting oxide that is a promising material for a multitude of applications. RuOx pH electrode has been studied for a long time. Here we would like to analyze some recently reported results. E. Tanumihardja et al. (Tanumihardja, Olthuis et al. 2018)\(^{44}\) -58.05 mV pH\(^{-1}\) for the RuOx nanorods for their pH sensing applications. Sol-gel derived RuOx sensing membrane exhibited a sensitivity of -65.11 mV pH\(^{-1}\)(Singh, Lou et al. 2019)\(^{45}\). S. Ali et al.(Sardarinejad, Maurya et al. 2015)\(^{46}\) reported high pH sensitivity ranging from -64.33 ~ -73.83 mV pH\(^{-1}\) for their sputtered deposited RuOx film with varying Ar/O\(_2\) gas flow ratio. Based on Pourbaix prediction, Ru-RuOx system could exhibit pH sensitivities of -59.1, -78.8, -98.5, and -118.2 mV pH\(^{-1}\) depending on redox reaction with different ion-exchange factors ‘x’. It is relatively easy to get pH sensitivity of -59 mV pH\(^{-1}\), as we discussed earlier. For higher-order ion exchange, high material purity is required. The dense pore formation in the RuOx with increasing Ar/O\(_2\) ratio resembles many isolated islands like structure, which makes the electron density and wave function discrete in nature. Therefore, high sensitivity in RuOx film is reasonable. A compact S-pbx plot for RuOx is presented in **Fig. S9A**.
The equilibrium potential of an electrochemical reaction involving Ta$_2$O$_5$ is impossible to measure directly in practice as the highly insulating property of Ta$_2$O$_5$. Therefore, Ta$_2$O$_5$ is suitable only for sensing membrane in ISFET. OCP and EGFET require low impedance sensing material. T. Akiyama et al. (Akiyama, Ujihira et al. 1982)\textsuperscript{47} reported a pH sensitivity of -56 mV pH$^{-1}$ in Ta$_2$O$_5$ ISFET. Poghossian et al. (Poghossian 1992)\textsuperscript{48} reported a high sensitivity of -80 ~ -85 mV pH$^{-1}$ in their Ta$_2$O$_5$ ISFET. Based on Pourbaix’s prediction, Ta$_2$O$_5$ could only exhibit a sensitivity of -59.1 mV pH$^{-1}$.

Our findings could explain the sensitivity of Ta$_2$O$_5$ film with deferent ion exchange and Pourbaix factor. A compact S-pbx plot for Ta$_2$O$_5$ is presented in Fig. S9B.

Zn-ZnO

Zinc based nanostructure are promising alternative materials for pH sensing. L. Maiolo et al. (Maiolo, Mirabella et al. 2014)\textsuperscript{49} reported sensitivity of -59 mV pH$^{-1}$ for as-grown ZnO nanowalls. Recently A. Scandurra et al. (Scandurra, Bruno et al. 2019)\textsuperscript{50} reported sensitivity of -83.7 mV pH$^{-1}$ for their as-grown Zn$_5$(OH)$_8$(NO$_3$)$_2$·2H$_2$O nanowalls whereas annealed sample showed only sensitivity of -27.1 mV pH$^{-1}$. Based on Pourbaix’s prediction Zn-ZnO system could ideally exhibit a sensitivity of -59.1, -88.6, and -118.2 mV pH$^{-1}$ depending on the ion exchange factor. Usually, an optimized annealing process improves the overall quality of a thin film or nanostructure, but sensitivity data does not reflect the same way. The degree of hydration in the sensing film has a significant role in determining the sensitivity. Spontaneous dissociation of H$_2$O harness H$^+$ and OH$^-$ ions inside the ZnO nanostructure. The pre-existing H$^+$ will enhance the overall sensitivity during the actual sensing process by triggering the higher-order ion
exchange in the interface. On the other hand, the high-temperature annealing completely removes the water content from the material, which resulted in lower sensitivity of -27.1 mV pH⁻¹. An S-pbx plot for Zn-ZnO is shown in Fig. S9C.

Cerium (Ce) based complex oxides

Lanthanides and their oxide have great potential as a pH sensing membrane. We would like to highlight two reported results where high sensitivity was observed. T. M. Pan et al. (Pan, Wang et al. 2018)⁵¹ reported high sensitivity of -89.81 mV pH⁻¹ in CeTi₃O₇ film. J. L. Her et al. (Her, Prasad Bag et al. 2018)⁵² reported sensitivity of -93.15 mV pH⁻¹ for Ce based complex oxide (Ce₂₋ₓSrₓ(Zr₀.₅₃Ti₀.₄₇)O₇). A compact S-pbx plot is presented for Ce-CeOₓ, considering a purely interfacial reaction CeOₓ and pH buffer, as shown in Fig. S9D. Other elements present in the structure may have minimal contribution towards electrochemical potential determining reaction.

Other material systems

There are few more reports where measured sensitivity is not very high, but still, the ion-exchange factor is more than 1 (x>1). Kao et al. (Kao, Chang et al. 2017)⁵³ reported how pH sensitivity of MgO film evolved from -30.17 mV pH⁻¹ to -60.37 mV⁻¹ by effective plasma treatment of the deposited film. Kuo et al. reported high pH sensitivity in WO₃ nanosheet (Kuo, Wang et al. 2018)⁵⁴. WO₃/V₂O₅ (Guidelli, Guerra et al. 2012)⁵⁵ mixed oxide system also exhibited high sensitivity during cyclic voltammetry and EGFET measurement. All these sensitivities could be explained with a similar understanding of different ion-exchange and Pourbaix factor.
Relevant Chemical Equilibrium Reactions for highly pH-Sensitive Materials

For ease of understanding, we presented here, the original chemical reactions and electrode potential from the book “Atlas of Electrochemical Equilibria in Aqueous Solution” (Pourbaix 1974) which are relevant and leads to high sensitivities in different pH-sensitive materials. The potential induced by metal oxide, oxide anions, hydrides is omitted intentionally from electrode potential expression as it will not contribute to overall pH response.

Graphene

\[ \Delta Z = 2(0 \rightarrow +2) \] [change of oxidation number in redox process]

\[ C + 2H_2O \leftrightarrow HCO_2H + 2H^+ + 2e^- ; E = E^0 - 0.0591 \text{ pH} \] (30)

\[ C + 2H_2O \leftrightarrow HCO_2^- + 3H^+ + 2e^- ; E = E^0 - 0.0886 \text{ pH} \] (31)

\[ \Delta Z = 4(0 \rightarrow +4) \]

\[ C + 3H_2O \leftrightarrow H_2CO_3 + 4H^+ + 4e^- ; E = E^0 - 0.0591 \text{ pH} \] (32)

\[ C + 3H_2O \leftrightarrow HCO_3^- + 5H^+ + 4e^- ; E = E^0 - 0.0739 \text{ pH} \] (33)

\[ C + 3H_2O \leftrightarrow CO_3^{2-} + 6H^+ + 4e^- ; E = E^0 - 0.0886 \text{ pH} \] (34)

Ir-IrOx

\[ \Delta Z = 3(0 \rightarrow +3) \]

\[ 2Ir + 3H_2O \leftrightarrow Ir_2O_3 + 6H^+ + 6e^- ; E = E^0 - 0.0591 \text{ pH} \] (35)

\[ \Delta Z = 4(0 \rightarrow +4) \]

\[ Ir + 2H_2O \leftrightarrow IrO_2 + 4H^+ + 4e^- ; E = E^0 - 0.0591 \text{ pH} \] (36)

\[ \Delta Z = 1(+3 \rightarrow +4) \]

\[ Ir_2O_3 + H_2O \leftrightarrow 2IrO_2 + 2H^+ + 2e^- ; E = E^0 - 0.0591 \text{ pH} \] (37)

\[ \Delta Z = 3(+3 \rightarrow +6) \]

\[ Ir_2O_3 + 5H_2O \leftrightarrow 2IrO_4^{2-} + 10H^+ + 6e^- ; E = E^0 - 0.0985 \text{ pH} \] (38)

\[ \Delta Z = 2(+4 \rightarrow +6) \]

\[ IrO_2 + 2H_2O \leftrightarrow IrO_4^{2-} + 4H^+ + 2e^- ; E = E^0 - 0.1182 \text{ pH} \] (39)
Pd-PdOx

\[ \Delta Z = 2(0 \rightarrow +2) \]
\[ Pd + H_2O \leftrightarrow PdO + 2H^+ + 2e^-; \ E = E^0 - 0.0591 \text{ pH} \] (40)
\[ \Delta Z = 2(+2 \rightarrow +4) \]
\[ PdO + H_2O \leftrightarrow PdO_2 + 2H^+ + 2e^-; \ E = E^0 - 0.0591 \text{ pH} \] (41)
\[ \Delta Z = 2(+4 \rightarrow +6) \]
\[ PdO_2 + H_2O \leftrightarrow PdO_3 + 2H^+ + 2e^-; \ E = E^0 - 0.0591 \text{ pH} \] (42)

At present, no relevant equation is available in the atlas, which could explain the experimental high pH sensitivity in the Pd-PdO system. As Pd is located close to the Ir in the periodic table, it may exhibit similar properties like Ir, and higher-order ion exchange is very susceptible.

Ru-RuOx

\[ \Delta Z = 3(0 \rightarrow +3) \]
\[ 2Ru + 3H_2O \leftrightarrow Ru_2O_3 + 6H^+ + 6e^-; \ E = E^0 - 0.0591 \text{ pH} \] (43)
\[ \Delta Z = 1(+3 \rightarrow +4) \]
\[ Ru_2O_3 + H_2O \leftrightarrow 2RuO_2 + 2H^+ + 2e^-; \ E = E^0 - 0.0591 \text{ pH} \] (44)
\[ \Delta Z = 4(+4 \rightarrow +8) \]
\[ RuO_2 + 2H_2O \leftrightarrow RuO_4 + 4H^+ + 4e^-; \ E = E^0 - 0.0591 \text{ pH} \] (45)
\[ \Delta Z = 3(+3 \rightarrow +6) \]
\[ Ru_2O_3 + 5H_2O \leftrightarrow 2RuO_4^{2-} + 10H^+ + 6e^-; \ E = E^0 - 0.0985 \text{ pH} \] (46)
\[ \Delta Z = 3(+4 \rightarrow +6) \]
\[ RuO_2 + 2H_2O \leftrightarrow RuO_4^{2-} + 4H^+ + 2e^-; \ E = E^0 - 0.1182 \text{ pH} \] (47)
\[ \Delta Z = 3(+4 \rightarrow +7) \]
\[ RuO_2 + 2H_2O \leftrightarrow RuO_4^- + 4H^+ + 3e^-; \ E = E^0 - 0.0788 \text{ pH} \] (48)
Zn-ZnO

$$\Delta Z = 2(0 \rightarrow +2)$$

$$Zn + H_2O \leftrightarrow ZnO + 2H^+ + 2e^-; \ E = E^0 - 0.0591 \text{ pH}$$

$$\Delta Z = 2(0 \rightarrow +2)$$

$$Zn + 2H_2O \leftrightarrow HZnO_2^- + 3H^+ + 2e^-; \ E = E^0 - 0.0886 \text{ pH}$$

$$Zn + 2H_2O \leftrightarrow HZnO_2^{2-} + 4H^+ + 2e^-; \ E = E^0 - 0.1182 \text{ pH}$$

Ta$_2$O$_5$

$$\Delta Z = 5(0 \rightarrow +5)$$

$$2Ta + 5H_2O \leftrightarrow Ta_2O_5 + 10H^+ + 10e^-; \ E = E^0 - 0.0591 \text{ pH}$$

At present, no relevant equation is available in the atlas, which could explain the experimental high pH sensitivity in the Ta$_2$O$_5$ system. To demonstrate high sensitivity in Ta$_2$O$_5$ system, we can simply use the concept of higher-order ion-exchange reaction, which already exhibits high sensitivity in other material systems.
A complete measurement setup: The whole measurement setup arranged on a desk including LabVIEW interface installed in PC, Keithly 2400 as SMU-1, NI DAQ and NI-PXI 4132 as SMU-2, homemade transducer box equipped with EGFET (CD4007 UBE) and CVCC-ROIC (OP-AMPs, current source, and sink), a height meter to immerse the LMPD probe in analyte with ease, an Ag/AgCl reference electrode (OHAUS STREF-1), and several pH buffer test solutions (pH 4 to 10). All the electrical instruments’ chassis is connected to a wrist strap ground port.
Materials for experimental Procedures: Photograph of (A) small glass bottles containing Gallium (on the left) and eutectic alloy EGaInSn, commercially known as Galinstan (on the right). (B) NIST standard pH buffer solutions (pH 4, 7, 10 from Hanna Instruments and pH 2, 5, 6, 8, 11, 12 from Alfa Aesar.) Ultrapure de-ionized (DI) water used for cleaning the electrode and other cleaning purposes. (C) PET containers for different pH buffer test solutions.
**Fig. S3.**

The highlight of individual components for experimental procedures: Photograph of (A) the Ag-AgCl reference electrodes. Measurement of the sensor probe performed mainly through a double junction reference electrode (OHAUS STREF-1) (B) Homemade transducer box equipped with a CVCC-ROIC and EGFET. Input-output leads connected using a BNC connectors for ease of connecting to the measurement instruments’ port (C) Photograph of the part of PCB showing the three important component (CD4007UBE on the top, LTC 6079 on the left and REF200 on the right) (D) Keithly 2400 LV source-meter as SMU-2 (mainly use it for measuring $I_{DS}$ and sweeping $V_{DS}$). (E) NI PXIe-1073 Chassis equipped with a NI-PXIe-6361 DAQ (mainly use DAQ for CVCC ROIC’s output voltage measurement), NI-PXI 4132 as SMU-2 (mainly use it for $V_{GS}$ and $V_{REF}$ bias sweep.) (F) Two electrode setup for potentiometric measurement, (left) LMPD probe and (right) Ag-AgCl electrode. (G) Precision HP E2378A multimeter used for OCP measurement (Movie S2).
Fig. S4.
Schematic illustration of the LMPD-EGFET measurement setup: SMU-1 is assigned to keep drain to source voltage (V_DS) constant at 0.5 V while at the same time measure the source to drain current (I_DS). SMU-2 is assigned to sweep the Ag-AgCl reference electrode (V_REF) voltage. With the synchronization of both SMUs, we measured the transfer characteristics (I_DS vs. V_GS) of EGFET in various pH buffer solutions (Movie S3). The E_ECP induced in the LMPD probe (liquid gate) is reflected in the MOSFET gate to source terminal; hence the parallel shift occurs in transfer characteristics with different pH.
Fig. S5.

Test of transfer and gate leakage characteristics of n-MOSFET: (A) Transfer characteristics ($I_{DS}$ vs. $V_{GS}$) of n-MOSFET in the linear region by suitably controlling $V_{DS}=0.5$ V. The same n-MOSFET is used as an extended gate FET for the LMPD sensor probe. (B) Test of gate leakage current ($I_{GS}$) while LMPD attached to the gate terminal of n-MOSFET. Gate leakage current of n-MOSFET measured for comparison. Gate leakage current is nearly one order higher with LMPD than that of n-MOSFET configuration.
Fig. S6.
CVCC ROIC: Schematic illustration of CVCC-ROIC for easy measurement of real-time LMPD sensor response in various pH buffer solutions. The number indicates the PIN of IC used (Numbers in black, blue and red for LTC 6079 Linear, CD4007UBE and REF200, respectively)
Fig. S7.
Test of linearity of read-out circuit and actual measurement of LMPD probe in different pH buffer: (A) Linearity characteristic of CVCC-ROIC ($V_{IN}$ is fed through the n-MOSFET gate using SMU-1 and $V_{OUT}$ is measured through input channel of DAQ card) (B) Screenshot of $V_{OUT}$ vs. time, measure of pH response of a LMPD sensor in pH buffer solutions of 4, 7, 10.
Fig. S8.
Sensitivity and linearity of LMPD from readout circuit: (A) $V_{OUT}$ vs. time characteristics measured from the output port of the CVCC-ROIC. The LMPD probe was carefully submerged into a pH buffer solution during measurement (Movie S1). The pH varies from 10 to 4 during measurement. (B) Twelve LMPD probes’ output voltage vs. pH were plotted with an error bar. The average sensitivity is $-97.01 \text{ mV pH}^{-1}$ with a standard deviation of $\pm 8.10$. 

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Fig. S9.

Sensitivity vs. compact Pourbaix and ion exchange factor (S-pbx) plot for different material system: S-pbx plot for (A) Ru-RuOx (B) Ta_2O_5 (C) ZnO and (D) CeOx (complex oxide) system. Available experimental sensitivities from the literature are plotted in terms of the Pourbaix factor (pb), which give a sense of deviation of the material quality from the ideal one. Details data are available in Table S1.
| M-M\textsubscript{2}O\textsubscript{3} or M\textsubscript{3}O\textsubscript{y} | Expt. Sensitivity (mV pH\textsuperscript{-1}) | Nearest Pourbaix Sensitivity (mV pH\textsuperscript{-1}) | ΔZ | Next nearest Pourbaix Sensitivity and ‘x’ mV pH\textsuperscript{-1}(x) | ‘pb’*** | Reference |
|---------------------------------|-----------------------------------------|-----------------|-----|------------------------------------------------|---------|---------|
| Ga-Ga\textsubscript{2}O\textsubscript{3} | -71 | -78.8* | 2 | -88.6 (3/2***) | 0.801 | This work |
| | -94.17 | -98.5* | 3 | -118.2 (6/3*) | 0.796 |
| | -110.78 | -98.5* | 3 | -118.2 (6/3*) | 0.930 |
| GaN-Ga\textsubscript{2}O\textsubscript{3} | -55.90 | | | | (24) |
| | -55.60 | -59.1* | 3 | -78.8 (4/3*) | 0.705 | This work |
| Graphene | -6, -8 | -14.7** | 4 | -29.5 (2/4**) | 0.203 | (27) |
| | -12 | -29.5** | 4 | -44.5 (3/4**) | 0.406 | (32) |
| | -20 | -44.4** | 4 | -59.1 (3/4**) | 0.451 | (33) |
| | -50 | -59.1** | 4 | -73.8 (5/4**) | 0.677 | (32) |
| | -98 | -103.4** | 4 | -118.2 (8/4**) | 0.829 | (28) |
| Ir-IrO\textsubscript{x} | -59 | -59.1* | 1,3,4 | -78.8 (4/3*) | 0.748 | (35) |
| | -73.7 | -78.8** | 2 | -88.6 (6/4**) | 0.831 | (35) |
| | -90 | -103.4** | 4 | -118.2 (8/4*) | 0.870 | (13) |
| | -115 | -118.2* | 2 | -118.2 (4/2*) | 0.964 | (36) |
| Pd-PdO | -28 | -29.5** | 2 | -59.1 (1*) | 0.473 | (40) |
| | -59 | -59.1* | 2 | -73.8 (3/2**) | 0.665 | (40) |
| | -64.71 | -73.8** | 4** | -88.6 (3/2**) | 0.730 | (39) |
| | -71 | -73.8** | 4** | -88.6 (3/2**) | 0.801 | (38) |
| Ru-RuO\textsubscript{x} | -58.05 | -59.1* | 1,3,4 | -73.8 (5/4**) | 0.786 | (S46) |
| | -65.11 | -73.8** | 3 | -78.8 (4/3*) | 0.826 | (S45) |
| | -73.83 | -73.8** | 3 | -78.8 (4/3*) | 0.833 | (S44) |
| Ta\textsubscript{2}O\textsubscript{5} | -56.0 | -59.1* | 5 | -70.92 (6/5**) | 0.789 | (S47) |
| | -85 | -94.5** | 5 | -106.38 (9/5**) | 0.799 | (S48) |
| CeO\textsubscript{x} | -89.81 | -98.5** | 3 | -118.2 (6/3**) | 0.759 | (S51) |
Table S1. Experimental sensitivities in connection with ion-exchange and Pourbaix factor

* Pourbaix formulation and prediction.
**Our prediction and addition supported by many experimental sensitivities in the literature.
***Pourbaix factor (pb) is calculated based on experimentally obtained sensitivity values for different sensing material with reference to the next nearest Pourbaix Sensitivity (not the nearest Pourbaix Sensitivity). Pourbaix factor (pb), give a sense of deviation of the material quality from the ideal one.

| (complex oxide) | -93.15 | -98.5** | 3 | -118.2 (6/3**) | 0.788 | (S52) |
|----------------|--------|---------|---|----------------|-------|-------|
| ZnO            | -27.1  | -29.5** | 2 | -59.1 (1*)     | 0.458 | (S50) |
|                | -59    | -59.1*  | 2 | -88.6 (3/2*)   | 0.665 | (S49) |
|                | -83.7  | -88.6*  | 2 | -118.2 (4/2*)  | 0.708 | (S50) |
Movie S1.
Liquid Metal Pendant Drop (LMPD) gently manipulated using a height meter with micrometer precision for immersion into the various pH buffer during measurement.

Movie S2.
OCP measurement using a HP-E2378A multimeter of EGaInSn LMPD in pH 10 buffer solution.

Movie S3.
Transfer characteristics \((I_{DS-V_{REF}})\) measurement of EGaInSn LMPD using Keithly and NI SMUs in pH 10 buffer solution.
Other Supplementary Information

Details calculation of Nernst Potential and relation with Subthreshold Swing (SS) of MOSFET

1. Nernst equation and Nernst potential

\[
E = E_0 - \frac{RT}{n_e F} \ln (a_{H^+})
\]

\[
= E_0 - 2.303 \frac{RT}{n_e F} \log(a_{H^+})
\]

\[\text{as} \ln x = 2.303 \log x\]

E= Potential of working electrode (non-standard)

\[E_0 = \text{Potential of reference electrode (standrad potential)}\]

(for Ag-AgCl Ref. electrode, \(E_0 \sim +0.740 \, \text{V}\))

R is the gas constant, \(R=8.314 \, \text{J mol}^{-1} \, \text{K}^{-1}\)

T= 298 K (25°C)

F is the Faraday's constant, \(F=9.6485 \times 10^4 \, \text{C mol}^{-1}\)

\(a_{H^+}\) is the activity of H⁺ ion which is basically pH of analyte

Calculation of Nernst potential

\[
2.303 \frac{RT}{F} = 2.303 \times 8.314 \times 298 \times \frac{9.6485 \times 10^4}{(J \text{ mol}^{-1} \text{ K}^{-1}) \times K} \frac{C \text{ mol}^{-1}}{C}
\]

\[
= 0.0591 \frac{J}{C} = 0.0591 \, \text{V} = 59.1 \, \text{mV}
\]

Nernst equation after calculation looks familiar as we often see it in text books:

\[
E = E_0 - \frac{0.0591}{n_e} \log (a_{H^+})
\]

2. Boltzmann Constant, Thermal Voltage and Sub-threshold swing (SS) of MOSFET

Boltzmann constant \(K_B = 1.380 \times 10^{-23} \, \text{J K}^{-1}\)

Thermal Voltage \(= \frac{K_B T}{q} = \frac{1.380 \times 10^{-23} \times 298}{1.602 \times 10^{-19}} \frac{(J \text{ K}^{-1}) \times K}{C}
\]

\[
= 0.02567 \frac{J}{C} = 0.02567 \, \text{V}
\]

Subthreshold Swing (SS) at 298 K(25°C) \(= 2.303 \times 0.02567 \, \text{V} = 0.0591 \, \text{V}\)
Certificate of Analysis (COA) of GaInSn (4N) and Ga (5N) provided by RICH-Metals, Inc., China

| Name                  | Spec.       | Pure | Lot No. | Standard No. |
|-----------------------|-------------|------|---------|--------------|
| Gallium-Indium-Tin     | GaInSn(68.5%-21.5%-10%Wt) | 4N   | Eutectic-Ga-GB1720-180305 |

### Impurity Content (ppm weight)

| Element | Test Result (max) | Element | Test Result (max) | Element | Test Result (max) |
|---------|-------------------|---------|-------------------|---------|-------------------|
| Cu      | 5                 | In      | 7                 | Al      | 7                 |
| Ag      | /                 | Ca      | /                 | Se      | /                 |
| Mg      | /                 | Fe      | 5                 | Pb      | 5                 |
| Sb      | 8                 | Cd      | 2                 | Sn      | /                 |
| Ni      | 3                 | Cr      | /                 | Na      | /                 |
| Zn      | 10                | As      | 3                 | Na      | 4                 |
| Mn      | /                 | Si      | /                 | /       | /                 |

NO:20200000

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Certificate of Analysis

| Name | Purity | Spec. | Total | Unit | Lot No. | Standard No. |
|------|--------|-------|-------|------|---------|--------------|
| Ga   | 5N     |       |       | kg   |         | Q7745074-7-840-2004 |

### Impurity Content (ppm weight)

| Element | Guarantee Value(max) | Test Result | Guarantee Value(max) | Test Result | Element | Guarantee Value(max) | Test Result |
|---------|----------------------|-------------|----------------------|-------------|---------|----------------------|-------------|
| Cu      | 0.06                 | In          | /                    | /           | Al      | /                    | /           |
| Ag      | /                    | Ca          | /                    | /           | Se      | /                    | /           |
| Mg      | 0.10                 | Fe          | 0.10                 | /           | Pb      | 0.05                 | /           |
| Sb      | /                    | Cd          | /                    | /           | Sn      | 0.10                 | /           |
| Ni      | 0.05                 | Cr          | /                    | /           | Na      | /                    | /           |
| Zn      | 0.10                 | As          | /                    | /           | Bi      | /                    | /           |
| Mn      | 0.05                 | Si          | 0.20                 | /           | /       | /                    | /           |

NO:20200000