A FLEXIBLE, MICROFABRICATED IMPEDIMETRIC FLUID TEMPERATURE SENSOR

Alex Baldwin, Trevor Hudson, Eugene Yoon, and Ellis Meng
University of Southern California, Los Angeles, USA

ABSTRACT

A novel impedimetric temperature sensor which utilizes the electrochemical impedance between two electrodes exposed to an aqueous solution to transduce temperature is presented. The solution resistance between electrodes is highly temperature dependent since ionic mobility increases with temperature. High-frequency electrochemical impedance can be used to accurately measure solution resistance, and therefore transduce fluid temperature. A temperature sensor composed of two platinum electrodes on a thin film Parylene C substrate exposed to fluid was designed, fabricated, and tested. Fluid temperature was transduced with high sensitivity (-59.33 Ω/°C) by measuring the impedance magnitude between electrodes at an appropriate frequency where phase was minimized. Compared to conventional platinum resistance temperature detectors (RTDs), our sensor achieved over 4× higher sensitivity and resolution (±0.02°C). Furthermore, the sensor is specifically designed for use in liquids, and features flexible, biocompatible construction for biomedical or microfluidic applications.

INTRODUCTION

State-of-the-art methods for measuring fluid temperature include thermocouples and resistance temperature detectors (RTDs) [1, 2]. Thermocouples utilize the Seebeck effect, in which a temperature-dependent voltage occurs at the junction of two dissimilar conducting elements [3]. They are generally made using nickel alloys, though occasionally platinum and rhodium are used to enhance stability, and have temperature sensitivities up to 60 µV/°C. However, thermocouples have low accuracy and precision, and generally cannot distinguish temperature changes less than 2°C. Semiconductor junctions can also be used as thermocouples, with sensitivities up to 110 mV/°C and resolutions as good as ±0.8°C [1]. Thermocouples require packaging to protect conducting elements from water intrusion and to act as a barrier shielding the body from non-biocompatible sensor material.

RTDs are conductive or semiconductive elements whose resistance changes with temperature. The most common commercial RTD (PT100) is made of bulk platinum wire and defined by a resistance of 100 Ω at 0°C and a temperature coefficient of 0.385%/°C [2]. Platinum RTDs can also be microfabricated on thin-film substrates, though the temperature sensitivity of thin-film platinum is lower than bulk material. Most metal RTDs use platinum due to its high linearity, but other metals such copper and nickel can be used as well. Laboratory-grade RTDs operate between -200°C and 1000°C with precision approaching ±0.001°C, although commercial RTDs are closer to ±0.03°C. The main drawbacks of platinum RTDs are low sensitivity and the need for encapsulation when used in aqueous solutions.

Semiconductor materials, such as silicon, germanium, and metal oxides, exhibit lower electrical resistance when operating at higher temperatures [1, 4]. These semiconductor RTDs, also known as thermistors, possess temperature coefficients exceeding -2%/°C and have comparable precision to metal RTDs. However, semiconductors corrode and disintegrate under chronic soaking in physiological fluid [5, 6].

An alternate approach to measure temperature changes in physiological fluid via measurement of the fluid's resistivity is investigated. The resistivity of an aqueous solution is temperature dependent due to increased ionic mobility at higher temperatures. This sensitivity exceeds the temperature coefficient of semiconductor materials (Table 1), with a reported temperature coefficient of -1.98%/°C for human cerebrospinal fluid [7]. Measuring solution resistivity using high-frequency electrochemical impedance enables highly sensitive fluid temperature transduction. Impedance spectroscopy was used to transduce the internal temperature of lithium ion batteries [8, 9]. However, until now, no one has demonstrated the use of impedance measurement to transduce temperature in bulk solution.

Table 1. Temperature coefficient of resistance (TCR) of metals and semiconductors which have been used in resistive temperature sensors, as well as several ionic solutions including human cerebrospinal fluid (CSF).

Material	Temperature Sensitivity (%/°C)
Platinum	0.392
Copper	0.430
Polysilicon	-2.5 to 0.1
Germanium	-2.0
1.32M (5%) NaOH	-2.01
7.9M (30%) NaOH	-4.50
2.95M (20%) KCl	-1.68
Human CSF	-1.98

THEORY

The impedance between two electrodes exposed to solution can be approximated by a Randles circuit [10] (Figure 1). This circuit consists of a charge transfer resistance R_{ct} and a double layer capacitance C_{dl} at each electrode-electrolyte interface, as well as the solution resistance R_s between the electrodes.

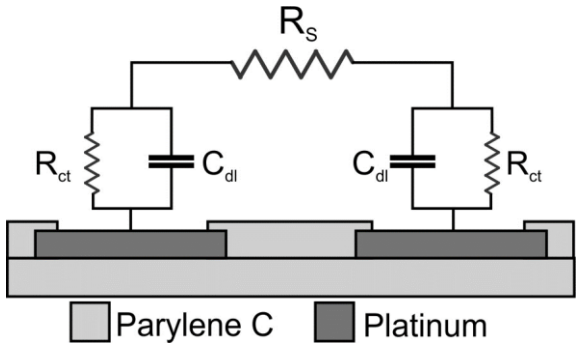

Figure 1: The electrochemical impedance between two electrodes consists of the solution resistance R_S, as well as a charge transfer resistance R_{ct} and double layer capacitance C_{dl} at each electrode interface. At high frequencies, the electrode-electrolyte interface is bypassed and impedance can be approximated as R_S.

R_{ct} describes the relationship between an electrode's overpotential v_0 and the resulting current due to faradaic reactions at the electrode surface. Assuming surface and bulk reactant concentrations are equal, the relationship between v_0 and the net current across the electrode-electrolyte interface i_{net} is given by the Butler-Volmer equation:

$$i_{net} = i_o\left\{e^{-\alpha_c nf v_0} - e^{(1-\alpha_c)nf v_0}\right\} \quad (1)$$

where α_c is a transfer coefficient which can range from zero to unity, n is number of electrons transferred, i_0 is the exchange current density, and f is equal to F/RT, where F is Faraday's constant, R is the gas constant, and T is temperature in Kelvin. At low overpotentials, the linear approximation of an exponential can be applied to equation 1, resulting in the following expression for charge transfer resistance:

$$i_{net} = \frac{-i_o nF}{RT} v_0 \qquad R_{ct} = \frac{dv_0}{di_{net}} = \frac{RT}{nFi_o} \quad (2)$$

This result implies a direct correlation between R_{ct} and temperature. Previously, charge transfer resistance was used to transduce the internal temperature of lithium ion batteries [8, 9]. However, the byproducts of faradaic reactions can be toxic [11], and many microelectrodes are too small for accurate measurement of charge transfer resistance. Therefore, electrochemical impedance measurement depends on C_{dl} and R_{ct}.

A double layer of electrostatically bound ions builds up at an electrode-electrolyte interface, leading to the formation of a capacitance C_{dl} [12]. Helmholtz, Gouy-Chapman, Stern, Graham, and others modeled this phenomenon, but the precise relationships between C_{dl} and temperature remains under active investigation and has not been fully characterized [13, 14].

Solution resistance R_S follows from a solution's conductivity, which is highly sensitive to changes in temperature. Electrolyte conductivity results from the movement of dissolved ions in response to an applied electric field. Bulk conductivity is proportional to ionic concentration, but a molar conductivity $\Lambda = G/c$ can be defined, where G is the bulk conductance and c is the molarity of ions [15]. As ionic concentration goes to zero, interionic forces disappear. This is known as a state of 'infinite dilution' and is useful for modeling conductivity in an aqueous solution. If an ion is modeled as a spherical charged particle within a continuous field of water and ionic mobility is defined as the limiting velocity per applied force, the conductivity at infinite dilution can be derived from Stoke's Law as

$$\lambda_0 = \frac{qF}{4\pi\eta r} \quad (3)$$

where λ_0 is conductivity at infinite dilution, q is ionic charge, η is water's viscosity, and r is ionic radius [16]. Only viscosity varies significantly with temperature; therefore, the temperature coefficient of a solution's conductivity at infinite dilution is inversely proportional to water's viscosity. Theoretical models for water's viscosity are generally inaccurate, but the following equation fits to empirical viscosity measurements within 1% accuracy for temperatures between 0 and 100°C and atmospheric pressure (0.1 MPa):

$$\frac{\eta}{10^{-6}\ Pa\ s} = \sum_{i=1}^{4} a_i \left(\frac{T}{300}\right)^{b_i} \quad (4)$$

i	a	b
1	280.68	-1.9
2	511.45	-7.7
3	61.131	-19.6
4	0.45903	-40.0

where η is in Pa·s and a and b are dimensionless, experimentally determined constants [17]. Using this formula, the infinite dilution temperature coefficient of conductivity can be shown to vary from -3%/°C to -1.5%/°C, with a value of -1.95%/°C at 37°C [18].

The Stoke's Law model of infinite dilution conductivity can be improved by including dielectric losses which occur due to the movement of charged particles. This results in the following:

$$\lambda_0 = \frac{qF}{4\pi\eta r + \frac{3}{8}q^2\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0^2 r^3}\tau_0} \quad (5)$$

where ε_0 and ε_∞ are the high frequency and low frequency limits of the solution permittivity and τ_0 is the Debye relaxation time [19]. Both the Debye relaxation time and water's permittivity are temperature dependent [20, 21], but changes in viscosity still drive the temperature sensitivity of ionic solution conductivity.

Interionic forces must be considered at concentrations above infinite dilution. These can be modeled by the Debye-Huckel-Onsager equation, leading to the following relationship between concentration and conductivity:

$$\Lambda = \lambda^0 - \left(\frac{z^2 eF^2}{3\pi\eta\left(\frac{2}{\varepsilon RT}\right)^{\frac{3}{2}}} + \frac{xz^3 eF}{24\pi\varepsilon RT\sqrt{\frac{2}{\varepsilon RT}}}\lambda^0\right)\sqrt{c} \quad (6)$$

where Λ is conductivity, c is electrolyte concentration in moles per liter, z is the valency number of each ionic species, e is the electron charge, and x describes the symmetry of an ionic species [22]. The temperature sensitivity of a solution decreases as ionic concentration increases, but this decrease remains negligible in most cases. For example, cerebrospinal fluid (CSF) has an ionic concentration of 295 mM, but there is only a 0.19% difference in its temperature coefficient compared to a solution at infinite dilution.

The above equations are valid for ionic solution composed of strong electrolytes. Weak electrolytes are much more complex, but in general their temperature coefficients will be much higher at high concentrations and approach that of strong electrolytes at low concentrations. This is due to the temperature dependence of a weak electrolyte's disassociation constant, leading to large changes in ionic concentration when temperature is altered. Intuitively, one would assume that ultrapure water would be either non-conductive and thus insensitive to changes in temperature or would have a sensitivity similar to an ionic solution at infinite dilution. However, despite resistivities greater than 18 MΩ·cm at room temperature, pure water does indeed conduct electricity. This conduction is mediated by a small fraction of water molecules spontaneously disassociating into hydroxide and hydronium ions. Ultrapure water acts similar to a very weak acid or a very weak base and exhibits a much higher sensitivity to temperature changes than ionic solutions, with a temperature coefficient ranging from 7.4%/°C at 0°C to 2.3%/°C at 100°C [23]. However, the addition of ppb levels of impurities will cause baseline conductivity to change by a much higher factor than changes in temperature, and the solution will soon resemble a typical ionic solution.

The predictable and highly sensitive relationship between R_S and temperature suggests the possibility of temperature transduction. By measuring electrochemical impedance at high frequencies, the electrode-electrolyte interface is bypassed and impedance consists only of R_S. Therefore, fluid temperature can be transduced using high-frequency electrochemical impedance (Figure 2). Solution resistance measurement is at its most efficient when phase is minimized.

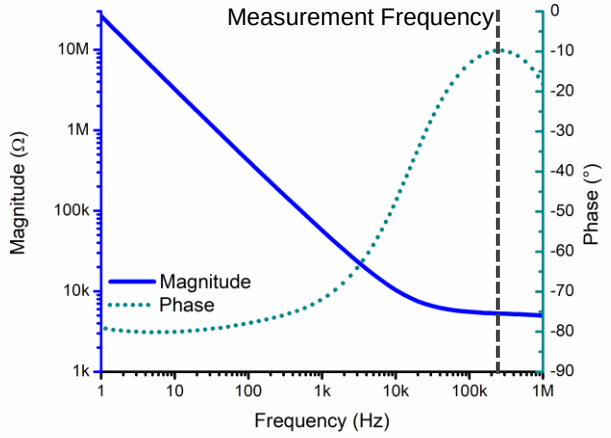

Figure 2. The magnitude and phase of temperature sensing electrodes, measured in 1×PBS. By measuring electrochemical impedance at the frequency where phase is minimized, solution resistance can be transduced.

EXPERIMENTAL DESIGN

We performed several experiments to demonstrate temperature transduction via high-frequency impedance. The temperature sensor used in these experiments consisted of a pair of platinum electrodes and a platinum resistor on a Parylene C substrate (Figure 3). The electrodes had exposed areas of 150 x 250 µm^2 with centers 750 µm apart. A platinum resistor, located 1 mm away from the electrodes on the same Parylene C substrate, was used as an RTD for benchmarking. The RTD consisted of a 25 µm wide serpentine trace and had a nominal DC resistance of ~450 Ω.

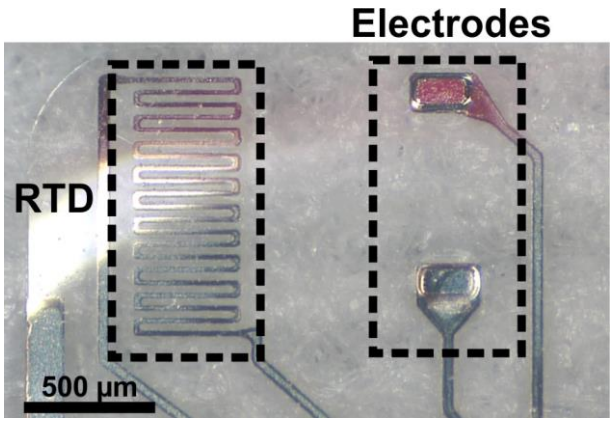

Figure 3: Impedimetric temperature sensing was tested using a pair of platinum electrodes on a Parylene C substrate. A microfabricated platinum RTD, fabricated on the same substrate, was used for benchmarking.

Sensors were primarily tested in phosphate-buffered saline (1× PBS), a common physiological fluid analog. 1× PBS is isotonic with cerebrospinal fluid and has a resistivity of 50 Ω·cm.

For electrochemical impedance spectroscopy (EIS) testing, sensors were sealed in glass vials filled with 1× PBS and placed in a water bath, which was heated to temperatures between 30 and 50°C. A Gamry Reference 600 potentiostat was used for EIS measurement (1 Hz – 1 MHz, 10mV$_{PP}$). For single-frequency impedance tests, solution was heated from room temperature (~20°C) to 50°C using a hot plate while a thermocouple/multimeter (Newport TrueRMS Supermeter, ±2°C accuracy) was used to monitor fluid temperature. Data was collected from impedance electrodes using an Agilent E4980A precision LCR meter at 0.1 V$_{PP}$ and from the RTD using a Keithley SourceMeter with 10 µA bias current. Impedance and resistance data was simultaneously collected and analyzed using a custom LabVIEW program.

RESULTS

EIS from 1 Hz to 1 MHz was measured from 30 to 50°C at 5°C temperature intervals (Figure 4). The results demonstrated a clear temperature dependency of impedance at frequencies from 1 to 100 kHz. The temperature coefficient was approximately -2%/°C, which matches reported temperature coefficient measurements in cerebrospinal fluid [7]. The discontinuities in the EIS graphs were likely a result of inadequate shielding by the chicken-wire Faraday cage. Although 10 kHz appeared to be the optimal measurement frequency due to its position in the center of the resistive range, single-frequency benchtop testing showed that measuring impedance at 100 kHz provided more consistent results.

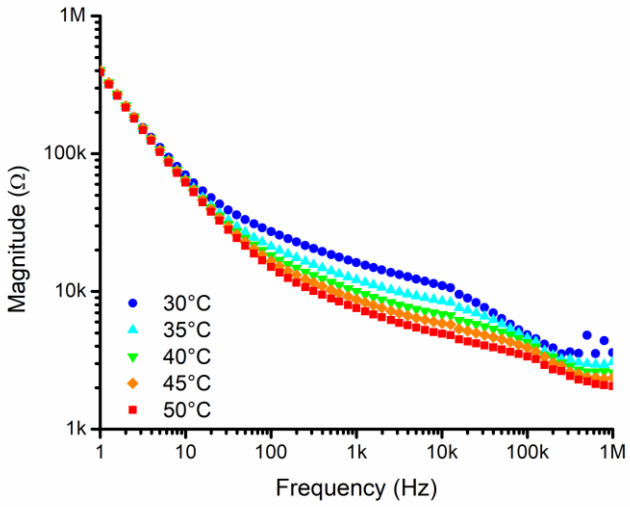

Figure 4: Electrochemical impedance spectroscopy of a pair of platinum electrodes at temperatures between 30°C and 50°C. As temperature increases, the impedance magnitude within the resistive range decreases.

The platinum RTD was calibrated by comparing its resistance to thermocouple measurements in 1× PBS, revealing a temperature coefficient of resistance of 1.21 Ω/°C. Temperature was then cycled between 20 and 50°C while simultaneously measuring impedance magnitude at 100 kHz and temperature using the RTD. The impedance magnitude correlated extremely well with temperature, with a temperature coefficient of -59.33 Ω/°C (Figure 5). Minimal hysteresis was observed over multiple cycles. Based on noise, 3σ resolution of impedance-based temperature sensing was measured to be ±0.02°C, compared to ±0.08°C for the platinum RTD.

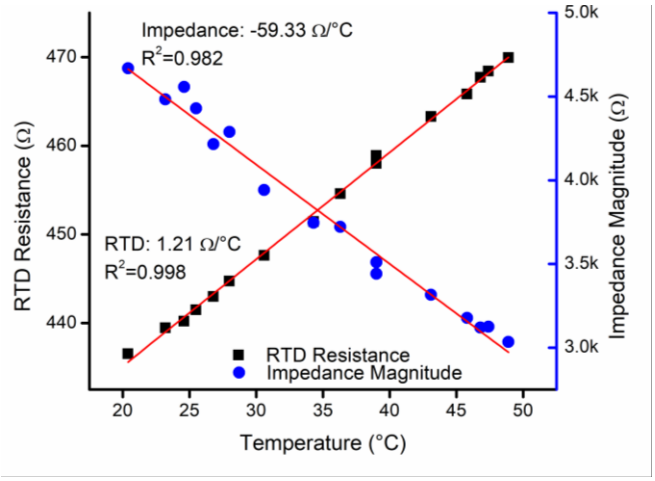

Figure 5: Impedance magnitude at 100 kHz was roughly linear with temperature, with a temperature coefficient of -59.33 Ω/°C and resolution of 0.02°C. This compared favorably to the RTD, which showed a temperature coefficient of 1.21 Ω/°C and a resolution of 0.08°C.

CONCLUSION

A novel method of measuring bulk fluidic temperature via electrochemical impedance was tested using a flexible, biocompatible temperature sensor. Results confirm theoretical predictions, and the impedimetric temperature sensor was able to measure sub-degree temperature fluctuations at a higher resolution than platinum RTDs, which are considered the gold standard for temperature transduction. Electrochemical impedance measurements are substrate-independent, and temperature measurement via electrochemical impedance can be implemented in any device with exposed electrodes in an aqueous solution. Future work will evaluate repeatable sensing in physiological fluids towards achieving chronic temperature monitoring in vivo, as well as exploring this technique's sensitivity to changes in ionic concentration and composition.

ACKNOWLEDGEMENTS

We would like to thank Dr. Brian Kim, Dr. Donghai Zhu of the Keck Photonics Lab, and all the members of the Biomedical Microsystems Lab for their help and support. This work was funded by the National Science Foundation under award EFRI-1332394.

REFERENCES

[1] P. Childs, J. Greenwood, and C. Long, "Review of temperature measurement," *Review of scientific instruments*, vol. 71, pp. 2959-2978, 2000.

[2] A. Tong, "Improving the accuracy of temperature measurements," *Sensor Review*, vol. 21, pp. 193-198, 2001.

[3] S. Kasap, "Thermoelectric effects in metals: thermocouples," *Canada: Department of Electrical Engineering University of Saskatchewan*, 2001.

[4] H.-M. Chuang, K.-B. Thei, S.-F. Tsai, and W.-C. Liu, "Temperature-dependent characteristics of polysilicon and diffused resistors," *Electron Devices, IEEE Transactions on*, vol. 50, pp. 1413-1415, 2003.

[5] A. Vanhoestenberghe and N. Donaldson, "Corrosion of silicon integrated circuits and lifetime predictions in implantable electronic devices," *Journal of Neural Engineering*, vol. 10, p. 031002, 2013.

[6] Y. Kanda, R. Aoshima, and A. Takada, "Blood compatibility of components and materials in silicon integrated circuits," *Electronics Letters*, vol. 17, pp. 558-559, 1981.

[7] S. B. Baumann, D. R. Wozny, S. K. Kelly, and F. M. Meno, "The Electrical Conductivity of Human Cerebrospinal Fluid at Body Temperature," *IEEE Transactions on Biomedical Engineering*, vol. 44, 1997.

[8] L. Raijmakers, D. Danilov, J. Van Lammeren, M. Lammers, and P. Notten, "Sensorless battery temperature measurements based on electrochemical impedance spectroscopy," *Journal of Power Sources*, vol. 247, pp. 539-544, 2014.

[9] R. R. Richardson, P. T. Ireland, and D. A. Howey, "Battery internal temperature estimation by combined impedance and surface temperature measurement," *Journal of Power Sources*, vol. 265, pp. 254-261, 2014.

[10] J. E. B. Randles, "Kinetics of rapid electrode reactions," *Discussions of the faraday society*, vol. 1, pp. 11-19, 1947.

[11] D. Merrill, E. Jeffrey, and L. Jay, "The Electrode—Materials and Configurations," *Essential Neuromodulation*, pp. 107-152, 2011.

[12] J. R. MacDonald, "Double layer capacitance and relaxation in electrolytes and solids," *Transactions of the Faraday Society*, vol. 66, pp. 943-958, 1970.

[13] A. A. Kornyshev, "Double-layer in ionic liquids: paradigm change?," ed: ACS Publications, 2007.

[14] M. Chen, Z. A. Goodwin, G. Feng, and A. A. Kornyshev, "On the temperature dependence of the double layer capacitance of ionic liquids," *Journal of Electroanalytical Chemistry*, 2017.

[15] R. A. Robinson and R. H. Stokes, *Electrolyte solutions*: Courier Corporation, 2002.

[16] M. Berkowitz and W. Wan, "The limiting ionic conductivity of Na+ and Cl− ions in aqueous solutions: Molecular dynamics simulation," *The Journal of chemical physics*, vol. 86, pp. 376-382, 1987.

[17] M. Huber, R. Perkins, A. Laesecke, D. Friend, J. Sengers, M. Assael, *et al.*, "New international formulation for the viscosity of H2O," *Journal of Physical and Chemical Reference Data*, vol. 38, pp. 101-125, 2009.

[18] A. Baldwin, L. Yu, and E. Meng, "An Electrochemical Impedance-Based Thermal Flow Sensor for Physiological Fluids," *Journal of Microelectromechanical Systems*, vol. 25, pp. 1015-1024, 2016.

[19] R. Zwanzig, "Dielectric friction on a moving ion. II. Revised theory," *The Journal of Chemical Physics*, vol. 52, pp. 3625-3628, 1970.

[20] H. J. Liebe, G. A. Hufford, and T. Manabe, "A model for the complex permittivity of water at frequencies below 1 THz," *International Journal of Infrared and Millimeter Waves*, vol. 12, pp. 659-675, 1991.

[21] W. Ellison, "Permittivity of pure water, at standard atmospheric pressure, over the frequency range 0–25 THz and the temperature range 0–100 C," *J. Phys. Chem. Ref. Data*, vol. 36, pp. 1-18, 2007.

[22] L. Onsager, "Theories of Concentrated Electrolytes," *Chemical Reviews*, vol. 13, pp. 73-89, 1933.

[23] T. S. Light, S. Licht, A. C. Bevilacqua, and K. R. Morash, "The Fundamental Conductivity and Resistivity of Water," *Electrochemical and Solid-State Letters*, vol. 8, p. E16, 2005.

CONTACT

Ellis Meng, ellis.meng@usc.edu