Low-cost Benzene Detection in High-density Networks

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***Abstract*—Project *needs a name* is a custom low-cost benzene sensor integrated onto a networked embedded system platform. In this project, titania nanotubes are synthesized to detect benzene [3]-[6] and a potentiostat circuit is designed and integrated onto a low-cost platform that can provide immediate notification of a leak occuring in a remote region. Sensor nodes use *Lo*ng *Ra*nge (LoRa) radio to communicate to a gateway node, 15km away that is connected to WiFi. Using *Amazon Web Services* (AWS) data is recorded using offering the end user a graphical user interface.**

***Keywords*—Benzene, electrochemical devices, internet of things, potentiostat, nanotubes**

I. MOTIVATION

Benzene gas is a natural, polluting constituent of petroleum and a dangerous volatile organic compound (VOC). This particular VOC is known for being carcinogenic and have harmful effects on bone marrow and red blood cells [16]. It is one of the few compounds known to cause cancer in humans, and, among airborne pollutants, it is the second biggest contributor to cancer risk in the United States. Over 6.7 million pounds of benzene are released into the air annually. However, benzene detection is challenging because of the distributed nature of benzene sources in industrial facilities and because its structure makes benzene difficult to detect inexpensively. Three types of end users need low-cost benzene detection: industrial customers who may release benzene, health researchers who need to to understand benzene exposure, and community organizations in regions likely to have elevated of benzene, such as communities affected by heavy traffic and industrial sites.

The United State Environmental Protection Agency in 2015 announced a new rule requiring refineries to monitor benzene concentrations at their fence line. The number of monitors required depends on size and shape of the refinery, but is estimated to be between 12-24 per facility [1],[2]. Current commercial benzene sensors such as MultiRAE Benzene or Tiger Select Benzene are expensive (about $5000 each) and are bulky. Other standard equipment including Gas Chromatography/Mass Spectrometry (GS/MS) and Ultraviolet Open Path Multi-Gas Analyzers (UV OPMA) are orders of magnitude more expensive than the aforementioned sensors and require expensive calibration and maintenance [7]-[10]. Such samplers are collected every two weeks and are sent to a lab for analysis. Thus, one to two months may elapse before a refinery knows it has a benzene-emission problem.

Consequently, a quick and cost-effective benzene screening method is needed. While this rule presently applies to 149 petroleum refineries, this approach may be extended to other facilities [11]. A low-cost benzene monitoring solution connected to a high-density network would allow for quicker leak detection. Current commercial benzene monitors are expensive and cannot be analyzed immediately. Not only can a cheap benzene detection system supply a proposed market for low-cost sensors, it may dramatically reduce health risks for neighboring communities by reducing exposure time.

Such a gas sensor coupled with a low-noise potentiostat circuit makes for a low-cost detection module that may not only detect benzene, but innumerous other analytes. This works based on the amperometric principle, which provides great analytics at an inexpensive cost [14].

Moreover, sensor cost is less than $100 and designed for manufacturability. With a market this large, the research laid out in this proposal can contribute not only to the benzene detection market but other electrochemical sensing applications as well.

II. SENSING BENZENE WITH TITANIUM DIOXIDE NANOTUBES

Over the past 15 years several researchers have been developing low-cost benzene sensors utilizing primarily thin metal oxide film, which provide instantaneous benzene concentration data [3]-[5]. However, these films have high operating temperatures and require a long stabilization period before operation. Fabricated sol-gel TiO2 sensors operated at 200-300C [6]. With operating temperatures this high, the sensor cannot be implemented in an embedded system.

The nano-sensing technology described in this project is constructed of self-aligned 3D titanium dioxide (TiO_2) nanotubes(T-NT) designed to operate at room temperature [6],[12], [13]. Self-ordered T-NT can be synthesized by a simple electrochemical anodization method developed by Dr. Mohanty [18] - [20]. In our project, the TiO_2 nanotubes will be formed by anodization of Ti foils (0.1 mm thick) in an electrolyte mixture of HF, H_2O and ethylene glycol. The anodization bath will be agitated under ultrasonic conditions with controlled temperature (100W, 42KHz, Branson 2510R-MT with homemade temperature control bath). A two-electrode configuration will be used for anodization. A flag shaped platinum electrode will serve as a cathode. The anodization will be carried out by varying the applied potential from 20 to 80 V using a rectifier (Agilent, E3640A). Varying the anodization potential can control the diameter of the tubes, and

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changing the anodization time can vary the length. Changing the water content can vary the wall thickness. The as-anodized TiO_2 will be annealed in oxygen or air at 500C for 2-6 h to increase its electrical resistance.

The resulting highly-ordered 3D TiO_2 nanotube array, shown in Fig. 1, creates a sensor with high surface area within a small amount of space. The TiO_2 nanotubes have excellent charge transport properties after annealing which makes them suitable for detecting binding events that occur on the nanotube face (i.e., detection of VOCs as they approach the sensor). Anodization is considered a robust, inexpensive, and easily scalable synthesis method to fabricate nanostructured metal oxides. In addition, site-specific and patterned growth using a photolithography technique was demonstrated in [21] using a large set of opportunities for complex packaging.

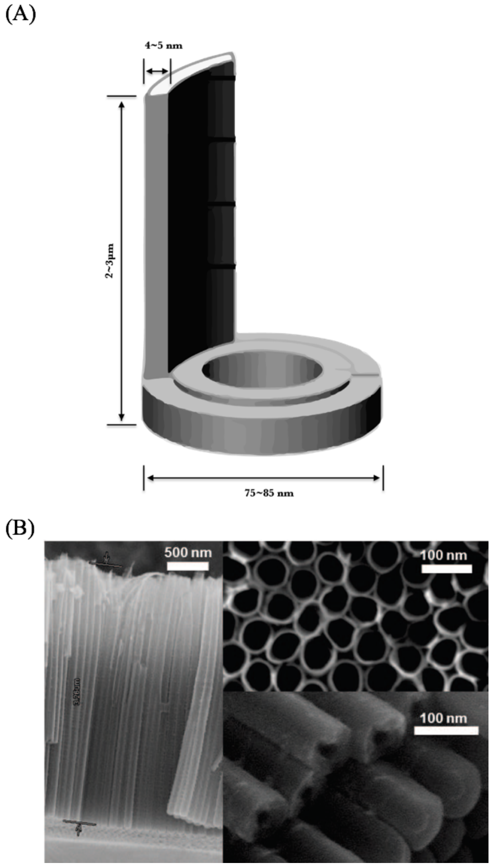

Fig. 1. Modified from [17]:
(A), The conceptual drawing of TiO2 nanotubes characteristics. (B), Scanning electron microscope images of TiO2 nanotubes. The lateral view (left) shows well-aligned nanotubes, the top view (right upper) shows circular shape of opened tip of nanotubes, and the bottom view (right lower) shows closed bottom part of nanotubes.

III. SYSTEM OVERVIEW

A LoPy microcontroller with wireless capabilities will be used in conjunction with the potentiostat circuit (sensor) and a gateway to create a fully functioning wireless sensor network. The LoPy is a compact triple network MicroPython enabled microcontroller (LoRa, WiFi, Bluetooth). It is housed on a custom PCB (sensor node) featuring USB and LiPo battery power, FTDI USB to serial converter, LiPo battery charger, MicroSD card slot, and a daughter board slot. The custom potentiostat (daughter board) is integrated onto the sensor node via pin headers. The potentiostat is an electronic instrument that controls the voltage difference between a Working Electrode and a Reference Electrode. Both electrodes are contained in an electrochemical cell or in this case T-NTs. A gateway is implemented using the same LoPy MCU and connecting it to AWS. DynamoDB is used as a fully managed cloud database for data collection.

IV. SENSOR NODE

The Internet of Things (IoT) is about interconnecting embedded systems, bringing together two evolving technologies: wireless connectivity and sensors. These sensor nodes are custom, independent LoPy expansion boards that are used to collect data from the potentiostat. This IoT system is networked together by a wireless radio protocol, LoRa. The networking protocol was selected based on the distribution of nodes and the amount of data to be collected. Sensor nodes are capable of deep-sleep mode, consuming only 25 uA. They can be powered with either USB or batteries. Each sensor node can be used with Lithium Polymer or Lithium Ion batteries.

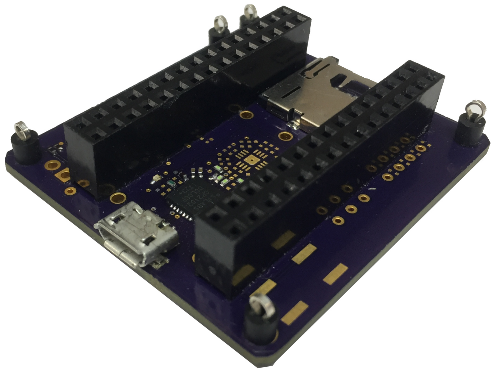

Fig. 2. Sensor Node

V. POTENTIOSTAT

Electrochemical sensors operate by reacting with monitored gas and producing an electrical current that is linearly proportional to the gas concentration. This potentiostat is based on a two-electrode configuration. When a gas comes in contact with the sensor, it passes through a thin membrane barrier to reach the electrode surface. The first electrode that the gas comes in contact with is the working electrode (WE). The WE is designed to optimize the electrochemical oxidation, (or reduction of the measured gas), and to generate a current flow that is proportional to the gas concentration. The performance of the sensor deteriorates over time due to the continuous electrochemical reaction of the changes in WE potential occurring on the electrode. To reduce deterioration while maintaining a constant sensitivity with a good linearity, a reference electrode (RE) is placed close to the WE. The reference electrode's purpose is to anchor the working electrode at the correct potential. In order for the RE to maintain a constant potential, no current should flow through it.

Fig. 3 shows a simplified potentiostatic circuit that is comprised of two amplifiers. There are small variations in the implementation of this circuit, but the function and the outcome are the same. The potentiostatic circuit's main purpose is to maintain a voltage between the reference electrode and the working electrode to control the electro-chemical reaction and to deliver an output signal proportional to the WE current.

When the sensor is exposed to the target gas, such as benzene, the reaction at the WE reduces, which diffuses out of the sensor. Ions and electrons are generated. The ions migrate through the electrolyte towards the working electrode. This process leaves a negative charge deposited on the working electrode. The electrons flow out from the working electrode through resistor R6 to the inverting input of the amplifier (U2). The amplifier is configured as a transimpedance amplifier, which converts the signal current from the WE into a voltage proportional to the applied gas concentration.

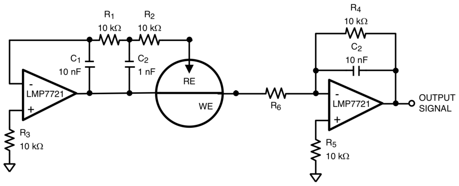

Fig. 3. Simplified Potentiostat

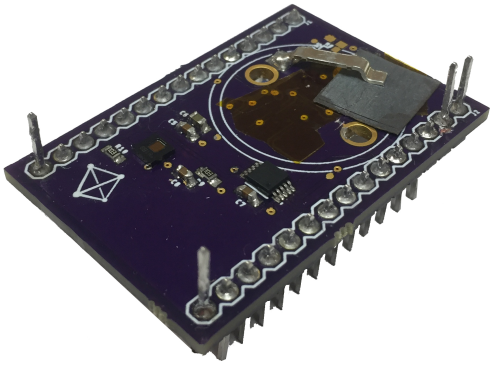

Fig. 4. Custom Potentiostat

VI. GATEWAY

The gateway is a node on a LoRa network that serves as an entrance to another network. In this case it is a sensor node reconfigured. The gateway is the MCU that routes traffic from a sensor node to AWS that is serving the database and GUI. LoRaWAN network architecture is typically laid out in a hub and spoke topology in which gateways is a transparent bridge relaying messages between end-devices and a central network server in the backend. Gateways are connected to the network server via standard IP connections while end-devices use single-hop wireless communication to one gateways.

VII. AWS SERVICE OVERVIEW

With AWS, we can handle the constant stream of data coming from several sensor nodes. This data can be a valuable source of information if it can be processed, analyzed, and visualized quickly in a scalable, cost-efficient manner. Potential customers can monitor performance and troubleshoot issues remotely, and in this case it means monitoring fenceline benzene concentrations. Facility managers can have some piece of mind with these tools.

The sample solution we have built becomes a monitioring and visualization dashboard for the LoPy gateway data. Fig. 5 shows a high-level architecture diagram showing the serverless setup to configure.

AWS Iot is a managed cloud platform that lets connected devices interact easily and securely with cloud applications and other devices. AWS IoT can process and route billions of messages to AWS endpoints and to other devices reliably and securely.

Amazon Kinesis Firehose is the easiest way to capture, transform, and load streaming data continuously into AWS from thousands of data sources, such as IoT devices. It is a fully managed service that automatically scales to match the throughput of your data and requires no ongoing administration.

Amazon Kinesis Analytics allows you to process streaming data coming from IoT devices in real time with standard SQL, without having to learn new programming languages or processing frameworks, providing actionable insights promptly.

The processed data is fed into Amazon QuickSight, which is a fast, cloud-powered business analytics service that makes it easy to build visualizations, perform ad-hoc analysis, and quickly get business insights from the data.

The most popular way for Internet-connected devices to send data is using MQTT messages. The AWS IoT gateway receives these messages from registered IoT devices. The solution in our project uses device data from HDC1080, a temperature and humidity sending sensor outputs in a JSON payload. This was done instead of benzene because the project doesn't have quick and readily available access to refineries' fencelines.

The AWS IoT rules engine allows selecting data from message payloads, processing it, and sending it to other services. You forward the data to a Firehose delivery stream to consolidate the continuous data stream into batches for further processing. The batched data is also stored temporarily in an Amazon S3 bucket for later retrieval and can be set for deletion after a specified time using S3 Lifecycle Management rules.

The incoming data from the Firehose delivery stream is fed into an Analytics application that provides an easy way to process the data in real time using standard SQL queries. Analytics allows writing standard SQL queries to extract specific components from the incoming data stream and perform real-time ETL on it. In this post, you use this feature to

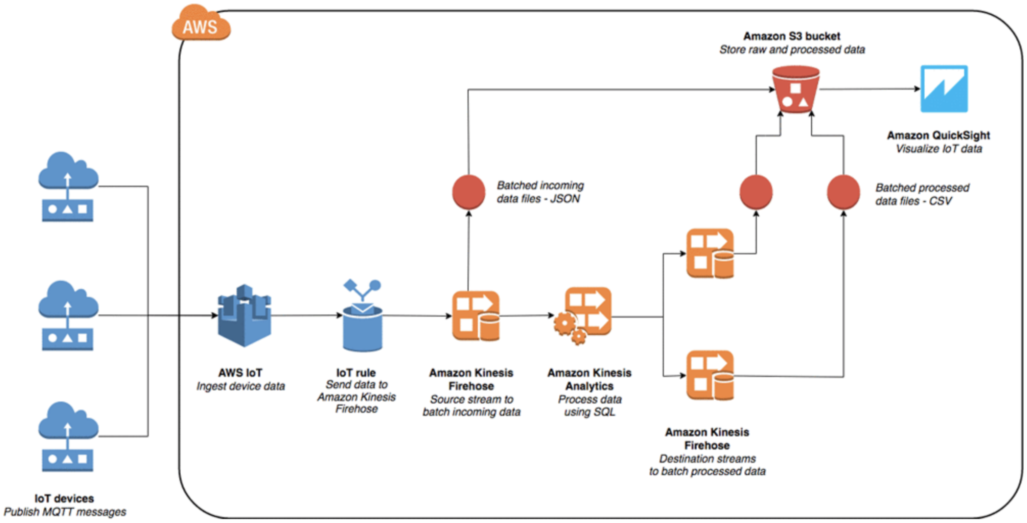

Fig. 5. AWS Service Overview

aggregate minimum and maximum temperature values from the sensors per minute. You load it in Amazon QuickSight to create a monitoring dashboard and check if the sensor nodes are behaving properly. You also extract every devices location, parameters such as temperature, humidity, and the time stamp in Analytics to use on the visualization dashboard.

The processed data from the two queries is fed into two Firehose delivery streams, both of which batch the data into CSV files every minute and store it in S3. The batching time interval is configurable between 1 and 15 minutes in 1-second intervals.

Finally, you use Amazon QuickSight to ingest the processed CSV files from S3 as a data source to build visualizations. Amazon QuickSights super-fast, parallel, in-memory, calculation engine (SPICE) parses the ingested data and allows you to create a variety of visualizations with different graph types. You can also use the Amazon QuickSight built-in Story feature to combine visualizations into business dashboards that can be shared in a secure manner.

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