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State-of-the-art monitoring of fuel acidity

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Abstract

Development of a novel iridium oxide (IrOx) based acidity sensor for off-line monitoring of fuel acidity is described. The sensor works in the potentiometric mode using an IrOx electrode as an indicating electrode and a Ag/AgCl or Ag/Ag_2O—reference electrode. The data show that the IrOx sensor responds to compounds present in fuel that have acid–base character. Using an off-line IrOx sensor, it is possible to determine the acidity of different fuels and discriminate between unstressed and thermally stressed fuels. It is possible to correlate the response of an IrOx sensor with the total acid numbers of different fuels. Experimental results also indicate that the low fuel conductance, the material used for sensor encapsulation, and/or the type of reference electrode may influence the response time of the IrOx sensor. Finally, the IrOx response has been demonstrated to be faster, better defined, more accurate and more reproducible than a glass electrode response for titrations of non-aqueous solutions.

Keywords: Iridium oxide; Sensor; Acidity; Non-aqueous solvents; Fuel; Total acid number

1. Introduction

Some acids can be present in aviation turbine fuels due to naturally occurring organic acids, the presence of some fuel additives, acid treatment during the refining process, and/or degradation/oxidation products of the fuel formed during service and thermal stressing [1]. In aviation fuel, the constituents considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, heavy metal salts, and additives, such as inhibitors and detergents. Significant acid contamination is not likely to be present because of the numerous quality control steps during the various stages of refining. However, trace amounts of acid can be present and are undesirable because of the consequent tendencies of the fuel to corrode metals and allow higher levels of dispersed water within the fuel [1].

The measurement of acidity is a difficult but important technique in the characterization of petroleum products. Information about acid content in fuel or lubricants is crucial because it is an indicator of the quality of these products; an acidic reading may suggest, for example, that an aircraft fuel has undergone thermal oxidation or that a lubricant has completely lost the added antioxidants and needs to be replaced [2]. The ability to continuously monitor these systems would provide an early warning for failure of these fluids. Perhaps more important than "user-level" specification testing [3–5] is the fact that the fuels processing industry must deliver neutral products compatible with fuel systems worldwide. In this regard, the process industry must create a product and then perform acid number testing [6]. If in-line monitoring could be performed more quickly and accurately than the off-line testing, process changes could be affected more readily, reducing waste and reprocessing.

Commercially available pH sensors are designed to conduct measurements in the aqueous phase. The measurement of acidity in organic solvent-based matrices like petroleum products is much more difficult due to their complexity and the fact that they are extremely non-conducting. Traditional electrochemical pH measurement technology is poorly suited for non-aqueous environments. Thus, non-aqueous pH measurements are meaningful only for monitoring the course of an acid–base titration or relative to some reference measurement made within the indi-

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vidual laboratory. Little, if any, confidence can be attached to absolute pH measurements in non-aqueous systems. Additionally, commercially available glass sensor electrodes are fragile and do not have the requisite stability, nor are they physically small enough to be easily incorporated into miniature reactors becoming more popular among research scientists [7–12].

The iridium oxide (IrOx) electrode has demonstrated superior long-term stability when compared to commercially available (glass electrode) and other experimental pH sensors (ion selective field effect transistors and other metal oxide electrode-based sensors) described in the literature [13–15]. Metal oxide electrodes (MOEs), in general, are inherently durable and suitable for miniaturization. However, based upon our empirical results, MOEs made by processes other than the thermal oxidation process are less stable (unpublished results). An IrOx pH sensor for aqueous applications has recently been developed and results suggest that IrOx sensors are superior to any other pH sensors on the market or in the published literature in terms of accuracy, long-term stability, sensitivity, reproducibility and response time [16]. This sensor is commercially available (SensIrOx, Inc.) and is fabricated using a proprietary process involving the thermal oxidation of iridium in a lithium carbonate melt. It has been demonstrated that lithium ions are inserted into the IrOx crystal matrix to form a new Li–IrOx compound. It is believed that it is the properties of this new compound that result in the improved performance of the sensor. As a result of their improved stability, the SensIrOx sensors do not require frequent calibration. They also can potentially be miniaturized and produced at a much lower cost. The SensIrOx sensor has shown excellent performance in aqueous solutions: the electrode exhibits excellent reversibility independent of the direction of the pH change or whether the pH is changed in small or large steps; it shows ideal Nernstian sensitivity (slope of 59.0 mV/pH), excellent reproducibility, and a response time on the order of seconds [16]. SensIrOx electrodes show good stability over a wide pH range, even at high temperatures [17], at high pressures [18], in aggressive environments, such as HF solutions [19], and fast response even in non-aqueous solutions [13]. Some preliminary work has also been done on using the SensIrOx electrode as a working electrode material for the development of acidity and basicity sensors for industrial lubricants [20]. These promising results motivated us to explore the use of the SensIrOx electrode for determining the acidity of aviation fuels.

The measurement of acidity in certain organic-based liquids, such as petroleum products is a difficult application due to the complex and non-polar (non-conducting) matrix. Solving the "low conductance problem" is the primary focus in the development of an acidity sensor for the petroleum products application. Petroleum products exhibit high electrical resistance because of their non-polar nature. Non-polar solvents have low ionic mobility and conductance due to the fact that they have low dielectric constants, extended ion pairing, and multiple ionic associations. Making electrochemical measurements in non-polar solvents is further complicated by the fact that they tend not to be very good solvents for salts and the resulting high electrical resistance can cause severe signal distortion. The use of microelectrodes can largely mitigate the resistance problem as they can allow effective electrochemical measurements in resistive media (e.g., in electrolyte-free liquids with low dielectric constants). However, for this work, since fabrication of the IrOx based indicator electrode in a micro-format was not considered a viable near-term option, fuel samples were simply diluted into a more polar solvent for analysis.

Currently, the measurement of Total Acid Number (TAN) in non-conducting fluids is performed by tedious, time consuming and solvent intensive methods (ASTM D 3242 [21] or D 664 [22]) based on titration. In these methods, the tested fuel sample is dissolved in a 1:1 mixture of toluene/isopropanol containing a small amount of water and titrated with standard alcoholic potassium hydroxide. In the D 3242 method, the end point is indicated by the color change of the added ρ-naphtholbenzein indicator solution. In the D 664 method, the inflection point during the titration is indicated potentiometrically using a glass indicating electrode and a calomel reference electrode. Clearly, a chemical sensor that could rapidly and reliably measure TAN in fuels and oils would be of tremendous use in specification testing, for monitoring/process control, as an R&D tool for additive development and for fuel thermal stability studies. An iridium oxide-based sensor (IrOx) may prove to be the best choice for these applications.

In this paper, efforts to develop an IrOx-based acidity sensor suitable for work in low conducting media, such as aviation fuel are described. Studies using the IrOx sensing system, are presented which demonstrate the detection characteristics in non-aqueous solutions and the feasibility of the IrOx (SensIrOx) sensor as a fast, accurate, real-time acidity off-line sensor for the testing of fuels. The development of a novel type of reference electrode is also described, where a thin porous polymeric film of cellulose acetate/cellulose acetate butyrate (CA/CAB) is used to protect the reference element from the fouling effect of fuel samples and facilitate the communication between the reference and working electrode.

2. Experimental

2.1. Chemicals and materials

All chemicals were obtained from Aldrich (Milwaukee, WI) and used without further purification. Water was deionized and purified using a Synergy Millipore water purification system. Fuel samples (Table 1) were obtained from the fuels branch of the Propulsion Directorate at Wright-Patterson Air Force Base. The fuel samples were identified using common Air Force nomenclature and reflect their content and properties that are proprietary.

The IrOx electrodes were obtained from SensIrOx, Inc. (Columbus, OH). The manufacturing process for these electrodes has been described previously with a detailed compositional analysis of the iridium oxide thin film [16]. The fabrication process involves the thermal oxidation of an iridium wire in a lithium carbonate melt. Various materials were tested for sensor encapsulation. These included: Eccobond 55 epoxy (Emerson & Cuming, Billerica, MA), polyimide resin (Restek, Bellefonte, PA), glass powder 7556 (Corning, Corning, NY),