ARTICLE IN PRESS
SOSI-13128; No of Pages 4
Solid State Ionics xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

All-solid-state sensors used in drilling muds to prevent H_2S gas evolution on oil wells

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ARTICLE INFO

Article history:
Received 7 May 2013
Received in revised form 24 September 2013
Accepted 21 October 2013
Available online xxxx

Keywords:
All-solid-state reference electrode
pH sensor
Ion-selective sulfide sensor
Potentiometric sensors

ABSTRACT

During oil or water drilling, the evolution of gaseous hydrogen sulfide (H_2S) may occur. A better solution would be to prevent the evolution of the gas by simultaneously measuring the presence of sulfide ions (S^{2-}) in the drilling mud and the pH, sulfide ions being predominantly under gaseous H_2S form when pH is smaller than 7. We proposed then to perform in situ measurements, using a potentiometric technique, to simultaneously record the presence of sulfide and the pH of the mud. In case of a rapid decrease of pH, human action could be done to rapidly increase the pH and to prevent H_2S evolution. A new type of all-solid-state reference electrode based on thick films of lithium lanthanum titanium oxide (LLTO) has therefore been developed. This reference electrode is associated with a solid state pH electrode and an ionic selective electrode for the detection of sulfide ions.

1. Introduction

The H_2S gas detection is a challenge for the oil drilling companies because of its high toxicity on oil drilling rigs. This gas is flammable, corrosive and particularly dangerous for human beings (it leads to respiratory problems under concentration as small as 200–300 ppm and may lead to death in some minutes under higher concentrations). To ensure full security of the working staff, it is then important to detect the presence of this gas in the areas of the rig, what is done at the time with gas sensors. The drilling fluid alkalinity maintains the sulfide species onto the basic form: the ion sulfide S^{2-} and its detection can be measured in situ with potentiometric sensors.

These in situ measurements can prevent H_2S gas evolution by controlling the pH of the mud and the presence of sulfide ions.

Since oil or water rigs are not easy environments, it is necessary to develop robust and then all-solid-state electrochemical systems to be inserted in the flowing mud. This means developing all-solid-state pH and sulfide sensors with an all-solid-state reference electrode with no clogging, resistant to abrasive and chemically aggressive fluids (mud pH is usually around 11–12).

In collaboration with Geoservices, a French society from the Schlumberger group, our team currently works on the development of an all-solid-state system of sensors with a pH sensor which is made of an antimony pH electrode and a sulfide sensor combined with a reference electrode. The absence of commercialized all solid-state reference electrode leads us to develop a new type of such reference electrode based on an oxide ceramic. The characteristic of this reference electrode will be presented in this paper (stability in aqueous solutions as well as in drilling mud) and its advantages compared to the commercialized reference electrodes.

The pH sensor and the ion-selective sulfide sensor combined with the all-solid-state reference electrode we developed will also be presented. Their characteristics such as the response time, the sensitivity of these sensors, their stability in aqueous and mud media will be discussed. The advantages of such in situ detection on oil and water wells will be developed.

2. Experimental method

2.1. Electrodes preparation

2.1.1. Solid state reference electrodes manufacturing

The procedure used for the preparation of the all-solid-state reference electrode has been highly inspired by the ceramic coating process developed by Barrow et al. at the Datec Coating Corp. [2] The so-called Datec® process is a method for producing thick ceramic films by a dip coating process.

The all-solid-state reference electrodes are prepared by depositing a thick film of lithium lanthanum titanium oxide called (LLTO) onto an alumina plate (96%, Anderman Ceramics) by dip coating. A silver wire 0.5 mm diameter (Strem Chemical) and silver glue (Epotechny, France) are used for the internal reference electrode.

2.1.2. LLTO film preparation of the precursor and the composite solutions

A dip-coater DC/D/LM from KSV (Finland) has been used for preparing thick films of LLTO. Two coating solutions have been prepared, a precursor solution and a composite solution. The so-called "precursor

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0167-2738/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.ssi.2013.10.045

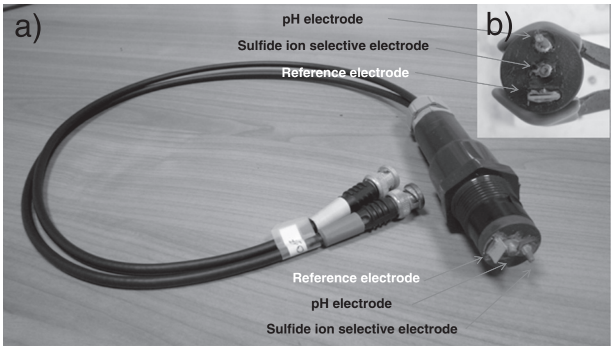

Fig. 1. Picture of the industrial combined sensor for pH and sulfide measurements.

solution" is made of a solution containing all the cations which after heat treatment in air should give LLTO powder. The "composite solution" is made of LLTO powder dispersed in the precursor solution of LLTO. These two solutions are used for preparing thick ceramic films. The detailed procedure was published previously [3].

The composite solution is prepared as follows: 20 wt.% of $Li_{0.3}La_{0.56}TiO_3$ powder is dispersed slowly in the above obtained LLTO precursor solution. The $Li_{0.3}La_{0.56}TiO_3$ powder is synthesized by a modified Pechini-type method, as described previously [4].

2.2. Antimony pH sensitive electrode

Antimony pH electrode was used for pH measurements at room temperature.

An antimony wire of 2 mm diameter and 20 mm length (Goodfellows, France) was attached by soldering to a silver wire. Different oxidation techniques were performed, in particular anodic oxidation in KOH (1 mol/L) with Radiometer Potentiostat PGZ 301 with platinum counter electrode and an Hg/HgO reference electrode. The antimony electrode can also be used only after oxidation in air. Calibration of the antimony electrode was previously performed in buffer solutions of pH 2, 4, 7 and 10 and in KOH 1 mol/L. Since the response of the electrode is not linear in such a large pH domain investigated, a cubic regression has been used for standardization.

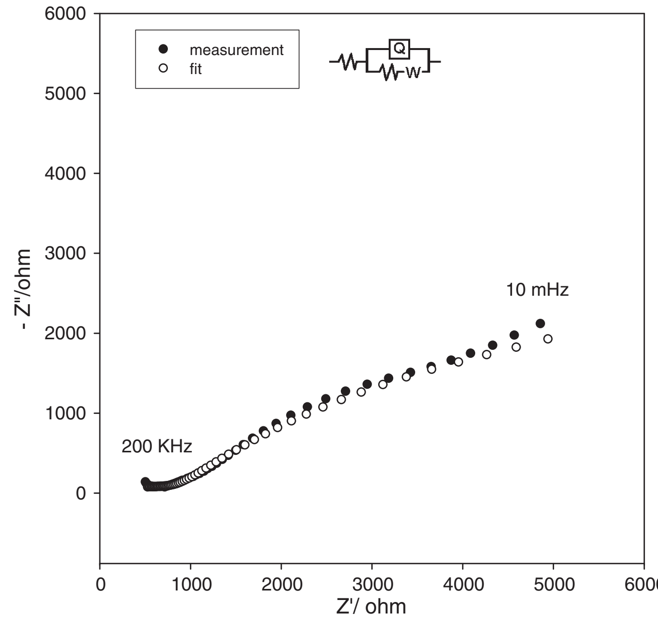

Fig. 3. Nyquist plot of impedance of the all solid state LLTO electrode buffer solution (pH 10 at 25 °C; $V = 20$ mV rms, and result of fitting using the B. Boukamp program).

2.2.1. Sulfide sensitive electrode

A silver wire (1.5 mm diameter, 100 mm length from Strem Chemicals) is embedded in Araldite glue. Typically, the silver end is sulfurized in sodium sulfide solution in molar KOH (1 mol/L) with a Radiometer Potentiostat (Pt counter electrode and Hg/HgO reference electrode) by applying a more positive voltage than the equilibrium voltage (about −500 mV/Hg/HgO during 20 min). A chemical sulfurization can also be performed in sodium sulfide without any electrochemical step.

2.3. Industrial sensors

Antimony electrode and the all-solid state reference electrode were embedded in Araldite glue (BASF) to form a cylindrical single sensor.

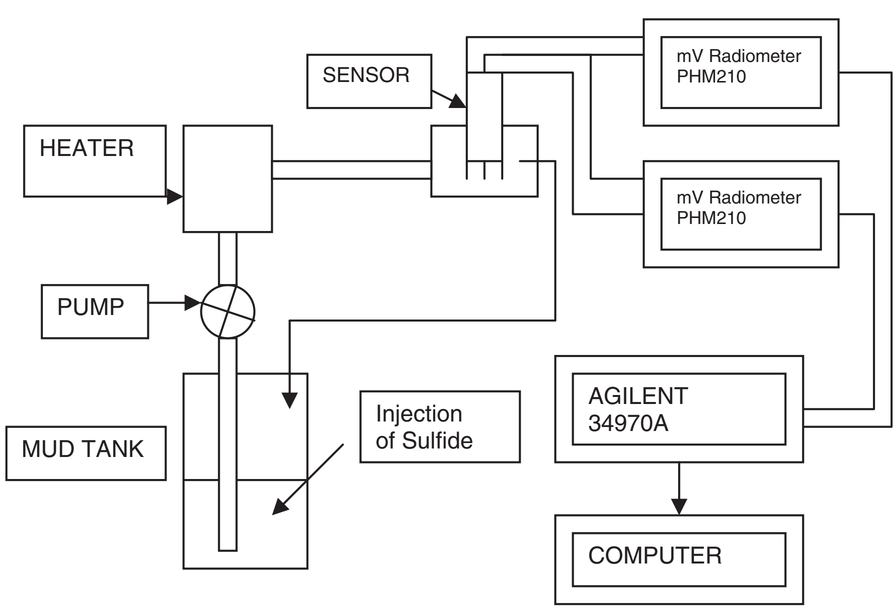

Fig. 2. Experimental setup showing the mud vessel (10 L), the pump, the heater and the data acquisition unit.

Please cite this article as: C. Bohnke, et al., Solid State Ionics (2013), http://dx.doi.org/10.1016/j.ssi.2013.10.045