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Research paper

Characterization of electrical properties of organic-rich shales at nano/micro scales

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ABSTRACT

A new experimental protocol is explored to characterize electrical properties of hydrocarbon-bearing mudrocks at nano/micro scales. Two current flow regimes of peak force - tunneling atomic force microscopy (PF-TUNA) have been used: (1) the vertical out-of-plane current regime with hundred micrometer diameter top electrodes obtains homogenized conductivity quantitatively, (2) the horizontal in-plane current regime was shown powerful to visualize the conductive paths (related to connectivity and tortuosity) for heterogeneous and anisotropic shales. Results show that the approach works well with one to two layers of adsorbed water (25–55% relative humidity) under low frequency (0.5–20 Hz) for shale rocks. Current maps with sub-nanometer resolution emphasize the dominant role of hydrated ions associated with the hydrophilic clay minerals in driving the dielectric response of shales, while conductivity of pyrite and kerogen cannot be neglected for mature organic-rich shale conductive network. The acquired I-V curves at microscale provide a reliable mean to evaluate homogenized conductivity of such multiscale multi-component heterogeneous material under controlled environmental conditions. The procedure discussed herein serves as a complement for fine grained rocks and minerals of ionic-electronic hybrid conductive mechanism under partially water saturation. These results can be used to develop accurate electrical models, specifically for shale rocks with heterogeneous and sophisticated microstructure. The methodology can be also extended to other micro- or meso-porous geomaterials such as cementitious and bituminous nanoporous media.

1. Introduction

Shale – a naturally formed geocomposite with ultra-low permeability – has received widespread attention, due to its vast hydrocarbon reserves and potential economical production rate following hydraulic fracturing (Bousige et al., 2016; Wang et al., 2016). Organic rich shale, a nanoporous material with mainly micropores (<2 nm) and mesopores (2–50 nm), contains clay and organic matter (e.g. kerogen) different from conventional reservoirs (Kuila and Prasad, 2013). Studies have shown that dispersed organic matter can trap carbon dioxide in an adsorbed state, therefore, organic-rich shales can become a natural candidate to sequester CO_2 as the gas wells are depleted (Kang et al., 2011). Shales with large amount of clay (large specific surface area, SSA leading to high cation exchange capacity, CEC to adsorb a large amount of ions) inside, has the potential to be long-term storage of high-level long-lived nuclear wastes (Cosenza et al., 2007, 2008, 2015). For the evaluation of subsurface resources as well as the safety assessment of waste disposals and CO_2 sequestration, it is desirable to have non-invasive tools to monitor in-situ petrophysical parameters (e.g. porosity, permeability, water content). For decades, scientists and engineers have been investigating storage and transport mechanisms in geological porous media such as reservoir rocks. Electrical resistivity was the earliest, the most important, and most frequently measured physical property of rocks (Bassiouni, 1994; Telford et al., 1990). Low-frequency and direct current (DC) resistivity were demonstrated promising to monitor the water content of clay-rich materials (Cosenza et al., 2007). However, the interpretation of resistivity data is complicated by many geological parameters such as porosity, fluid salinity and resistivity of different minerals constituting rock especially clay particles.

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Electrical experiments of shale can be traced back to Waxman and Smith's model (Waxman and Smits, 1968) and "dual-water" model (Clavier et al., 1984) for shaly-sand. Revil and co-workers (Cosenza et al., 2007; Jougnot et al., 2010; Revil, 2012; Revil et al., 1998; Revil and Leroy, 2004) did theoretical and experimental work systematically after that, based on assumptions that grains are covered by an electrical double layer (comprising Stern layer and diffuse layer) and submerged in a background electrolyte. They concentrated on standard core samples in laboratory, which can be used for well log interpretation of shaly sands, argillites and other clay-rocks.

However, most electrical experiments of reservoir rocks aforementioned are performed on brine saturated samples in the laboratory. One reason is that it could simulate the in-situ environment around geo-materials underneath and could control the salinity and saturation to investigate the relationship between conductivity and different parameters (Revil, 2016). The other reason often neglected is that, for normal standard core samples, no observable current or voltage signals can be detected if without being saturated using the traditional electrical set up in the lab. This approach is well-suited for sandstone (Archie, 1942), carbonate rocks (North et al., 2013), shaly sands (Revil et al., 1998), cement and siltstone (Jang et al., 2016; Rajabipour and Weiss, 2007) because of their larger pore size, which can be easily saturated even under ambient pressure. But high pressure is required to saturate fine-grained mudrocks and shales due to their extremely low permeability (~10 nd, Nano Darcy), resulting in pressure-related micro cracks and textural changes. Performing this procedure at the macroscale can be a time consuming process that can last from several weeks to several months (Revil et al., 2013; Woodruff et al., 2014, 2015).

Considering the multi-scale characteristic sizes (~1 nm–~100 μm) of multiphase in shales (e.g., clay phase, calcite phase, organic matter, etc.) (Abedi et al., 2016a, 2016b) and their intrinsic high resistivity, the assessment of their electrical properties entails the use of nanoscale testing methods with high current sensitivity such as tunneling atomic force microscopy (TUNA). Herein we employed a new laboratory approach to investigate electrical properties of organic rich shales at small scales for the first time. The invention of atomic-force microscope (AFM) in 1986 by Binnig et al. (Binnig et al., 1986) could be traced back to the first member of AFM family - scanning tunneling microscope (STM) in 1982 (Binnig et al., 1982). AFM precisely measures interactive forces between tip and substrate by recounting cantilever deflection in the perpendicular direction as the tip reaches the surface and retracts from it. Thus, topography mapping is observed accordingly, which is beneficial to compare with scanning electron microscope (SEM) image by distinguishing different phases for heterogeneous materials like shale (Eliyahu et al., 2015; Emmanuel et al., 2016; Javadpour et al., 2012). Measurements of conductivity at the nanoscale were initially obtained by a contact mode AFM furnished with a conductive tip and a current-sensing unit by conductive - atomic force microscopy (C-AFM). PF-TUNA(Peak Force - tunneling atomic force microscopy, Bruker: Dimension Icon®) which has more precise current sensitivity (pA to nA) compared with C-AFM(nA to μA) has been successfully applied in electrical characteristics of polymer (Cicco et al., 2015; Jafarzadeh et al., 2014), polyimide (Hu et al., 2012), hybrid composites (Gutierrez et al., 2014), lithium-ion batteries (Cañas et al., 2013; Kalinin et al., 2011), exploring local ionic dynamics in functional oxides at the nanoscale (Strelcov et al., 2013) and investigating conductive paths in metal-insulator composite (Luo et al., 1996). PF-TUNA uses tapping mode which contacts sample surface intermittently. This contact mode not only increases the service life of probes but also reduces the modification of sample surfaces even after scanning many times, thus making sure that the results are stable and repeatable (Li et al., 2011).

In this paper, we will take shale rocks as an example, to illustrate how PF-TUNA works for nanoporous geomaterials and we discuss sample preparation, two electrical experiment regimes and how conductivity is influenced by adsorbed water. Anisotropic ratio are determined and conductive paths can be visualized for heterogeneous and anisotropic materials.

2. Experiments

2.1. Properties of shale sample

The main shale sample used here comes from the Haynesville formation which is located in Texas-Louisiana Salt Basin with a strong vertical transverse isotropy (Woodruff et al., 2015). According to shale layered texture, X1 is the direction inside of or parallel to bedding plane, while X3 is perpendicular to bedding plane. Mineralogy determined by X-ray diffraction (XRD, Research & Analytical Laboratories, Inc.®), total organic carbon (TOC), Rock-Eval pyrolysis and maturity testing of source rock analyses (Nutech Energy Alliance Corporation®) are listed in Table 1 and 2. Mercury injection capillary pressure (MICP, PoroLabs, Inc.®) test shows porosity 3.2%, grain density 2.63 g per cubic centimeter (g/cc), bulk density 2.55 g/cc, "stressed" permeability to air (Swanson) 20nd (Nano Darcy), and the median pore throat radius is 3 nm with pore throat size distribution (about 30% of pores having diameter less than 2 nm and 99% of pores having diameter less than 50 nm) shown in Fig. 1.

2.2. C-AFM geometries (vertical and horizontal)

There are two geometries possible to measure electrical properties (Mativetsky et al., 2014) by PF-TUNA or C-AFM (Fig. 2): vertical geometry to measure out-of-plane current and horizontal geometry to measure in-plane current. In vertical geometry (Fig. 2a), the conductive cantilever serves as one electrode whereas conductive adhesives (silver epoxy, 0.4 ohms/sq/mil) between

Table 1
Mineral contents determined by X-ray diffraction (XRD, Research & Analytical Laboratories, Inc.®) of Haynesville shale sample.

Composition	(Weight percent, wt. %)
SiO2 (Quartz)	23.1
CaCO3 (Calcite)	33.2
CaMg(CO3)2 (Dolomite)	7.7
KAl2(AlSi3O10)(F,OH)2(Illite)	25.8
(Fe,Mg)5Al(AlSi3O10)(OH)8 (Chamosite)	1.7
FeS2 (Pyrite)	1.4
NaAlSi3O8 (Albite)	6.2
Ca5(PO4)3(F,Cl,OH) (Apatite)	0.9
all inorganic	100

Table 2
Geochemical properties of Organic matter within Haynesville shale sample determined by Rock-Eval pyrolysis (Nutech Energy Alliance Corporation®).

S1 [mg free HC/g rock]	0.79
S2 [mg potential HC/g rock]	0.37
S3 [mg CO2/g rock]	0.3
Ro [VRr, vitrinite reflectance]	1.75
Tmax (°C)	495
TOC(wt.%)	2.77
Kerogen type	II