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Birnessite-clay mineral couple in the rock varnish: a nature's electrocatalyst†

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Hydrogen (H_2) energy is produced by electrochemically splitting water molecules, and if produced economically, it will bring a paradigm shift in the development of sustainable energy systems. Several attempts have been undertaken in recent years to produce better electrocatalysts for the water oxidation process, with a focus on oxygen evolution reaction (OER) processes. A lot of work has gone into designing effective manganese-based heterogeneous catalysts for the water oxidation process, and a number of synthesized manganese oxides have been shown to have good alkaline OER activity. With the first-ever description of a natural material (rock varnish) constituted of birnessite (δ-MnO_2) combined with clay minerals as a potential OER catalyst, the current work represents a typical scenario of the marriage between energy and the environment. This natural material having a current density of 10 mA cm^{-2} at a lower overpotential (η) of 312 mV and a Tafel slope of 46 mV dec^{-1} exhibits exceptional electrocatalytic performance on par or better than its synthesized Mn-based electrocatalysts. Rock varnish paves the way for developing highly active as well as stable manganese-based water oxidizing catalysts and may serve as a model for the biomimetic inspired synthesis of novel classes of MnO_2-clay based composite materials as efficient water electrocatalysts for our future clean energy needs.

1. Introduction

Rock varnishes are the dark, brown-coloured natural micro-coatings found on rocks in dry and semi-arid regions around the world.[1] These black-brown veneers are often made up of Fe and Mn oxides mixed with clay minerals,[2] and they form on the rock surfaces over time as a result of various environmental and chemical processes.[3] These enigmatic coatings have always been employed to create petroglyphs and have piqued the interest of archaeologists. Geologists, on the other hand, are always interested in learning more about how these varnish layers originate, examining their characteristics, and even assessing their paleoclimatic significance.[4] The abiotic hypothesis, which holds that small changes in pH can concentrate manganese in these layers *via* geochemical processes,[5] and the biotic hypothesis, which holds that bacteria and other microorganisms are responsible for manganese concentration,[6] have been proposed to explain the origin of rock varnishes. As a result, rock varnishes have kindled the curiosity of archaeologists and geologists working in various geographical locations around the world.[7,8]

Research on the mineral composition and geochemical analysis of rock varnishes have been published worldwide, but only a few studies on the semiconducting characteristics of these Fe/Mn oxide coatings have been reported.[9] Although manganese oxide is an abundant natural resource and is a low-cost material,[10] the electrochemical applications of manganese oxide present in the varnish layer have been overlooked. Manganese oxides occur naturally in both crystalline and amorphous forms, with MnO_6 octahedral units being found in the corners of crystalline layered or tunnelled formations.[11] The enormous surface area and porosity of these structural designs are advantageous in a range of applications, including heterogeneous catalysis, hazardous waste clean-up, rechargeable batteries, and supercapacitor production.[12]

Alternative energy sources are not a new concept for humans; however, energy has become the world's most important concern in the 21st century. Fossil fuel supplies are limited, and they are expected to be consumed by the middle of this century.[13] Particularly, when there is a push to reduce CO_2 emissions to alleviate the negative impacts of global warming, the search for alternate and clean energy resources has accelerated. Alternatively, processes, such as photocatalytic water splitting, have also been proposed as a possible technique for producing clean hydrogen from solar energy.[14,15] As a result of this debate, hydrogen generation has emerged as a vital

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