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Proton conduction in electrolyte made of manganese dioxide for hydrogen gas sensor

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Abstract: We propose a network model of oxygen-pairs to store and conduct protons on the surface of manganese dioxide with a weak covalent bond like protons stored in pressured ice. The atomic distances of oxygen-pairs were estimated between 2.57 and 2.60 angstroms in crystal structures of ramsdellite-type and lambda-type manganese dioxides by using protonated samples and inelastic neutron scattering measurements. Good properties for a hydrogen gas sensor using electrolytes made of manganese dioxides that contain such oxygen-pairs were confirmed experimentally.

Key words: hydrogen sensor, proton conduction, manganese dioxide, inelastic neutron scattering, network model of oxygen pairs, and weak covalent bond

Introduction

We reported a hydrogen gas (H_2) sensor using an electrolyte made of a nanometer-scale ramsdellite-crystal-type MnO_2 (RMO) in a wet condition with water that enables in-situ measurements of H_2 concentration over a wide range of 0.1-99.9% at room temperature [1]. In the report, the RMO powder was processed into a pellet to act as an electrolyte in the sensor for the measurement of H_2 concentrations, and various crystal structures of MnO_2 such as ramsdellite-type [2], lambda-type [3], beta-type, and gamma-type were tested for the electrolyte. As the result, the electrolyte made of the RMO showed a good response to H_2 and a low residue on the output voltage for sequential usages of the sensor system. We thought that such good properties of the RMO electrolyte were based on a unique proton conductivity of the RMO compared to that of other crystal structures of MnO_2. However, the mechanism of proton conduction in the RMO electrolyte was not clarified up to now. In this study, electrochemical properties of electrolytes made of different crystal structures of MnO_2 were investigated. And the RMO powder after its protonation was analyzed by an inelastic neutron-scattering (INS) study.

Experimental

Fig. 1 shows a schematic of the sensor, where the platinum (Pt) meshwork pieces attached to each side of the wide pellet (diameter: 2cm, thickness: 0.7mm) served as the electrodes and also as catalysts for the $H_2 \rightarrow 2H^+ + 2e^-$ dissociation. Voltages generated between the Pt electrodes were determined. The RMO and its protonated sample (PRMO) were prepared according to methods of past reports [4,5]. The INS study was performed on the High Resolution Medium Energy Chopper Spectrometer at the Intense Pulsed Neutron Source at the Argonne National Laboratory.

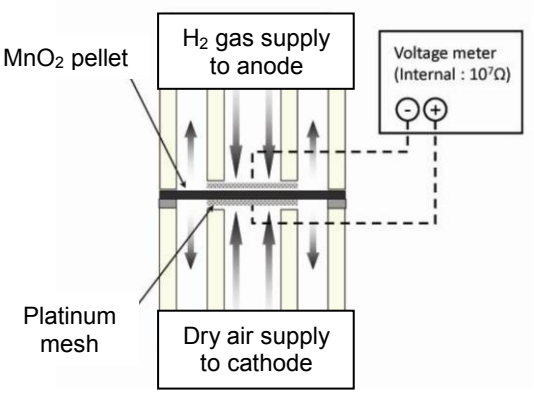

Fig. 1. Schematic of the hydrogen gas sensor system.

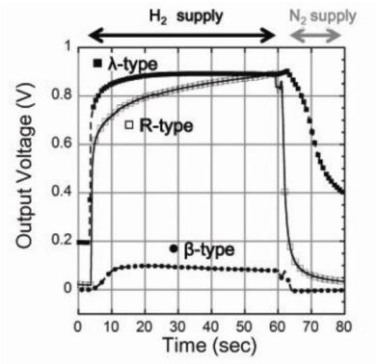

Fig. 2. Sensoring property of H_2 gas (99.9 vol. %); The H_2 gas and the N_2 gas (99.9 vol. %) were supplied alternately to the anode surface of various electrolytes made of different crystal structures of MnO_2.

Results and discussion

Fig. 2 shows that the electrolyte made of the RMO performed a good response and a low residual voltage. And the lambda-MnO_2 electrolyte also showed a good response, but the residual voltage was higher than that of the RMO electrolyte. Regarding the beta-MnO_2 electrolyte, both of the response and the output voltage were obviously lower than the others.

Fig. 3 displays the INS spectrum for the PRMO obtained from the RMO treated with acidic ultra-pure water of pH 1. Because the spectrum reminiscences the spectrum of hexagonal ice-Ih, the later is also shown for comparison. The spectra for water/ice can be divided for the intermolecular translational (below 50 meV) and librational (50 to 140 meV) bands, as well as intramolecular bending (around 200 meV) and stretching (around 400 meV) modes. A large shift of the first acoustical peak in the INS spectrum of PRMO compared to that for ice-Ih (at ~7 meV) indicate the absence of the bulk water in the PRMO sample. In the energy range of O-H stretching modes of the PRMO sample a broad peak is observed which can be well fitted with 2 Gaussians positioned at 366 and 410 meV. The later mode is clearly related to the O-H stretching modes in the interfacial or surface water. The peak at 366 meV should correspond to O-H stretching mode related to very weak covalent bond, which can be a consequence of very strong hydrogen bond constructed by another closely placed oxygen. Thus, this mode is probably due to stretching vibrations of O-H bond in O-H•••O arrangement, which has short O-O distance. The peak at 366 meV, indicates the existence of O-H•••O assembly with the O-O distance between 2.57 and 2.60 Å in the crystal structure of the PRMO; these values are estimated from the phenomenological dependence of the O-H stretching mode and O-O distance in ice [6]. Such short O-O distance of MnO_2 only exists in ramsdellite-type and lambda-type structures, and the other crystals of MnO_2 do not have such short O-O distances. Especially, networks of oxygen pairs which have atomic distances of O-O (*e.g.* 2.573 and 2.589 angstroms), were found along the specific axis of the crystal structure in the ramsdellite-type MnO_2. Other crystal-types of MnO_2 do not contain such network of O-O pairs in those ideal crystal structures.

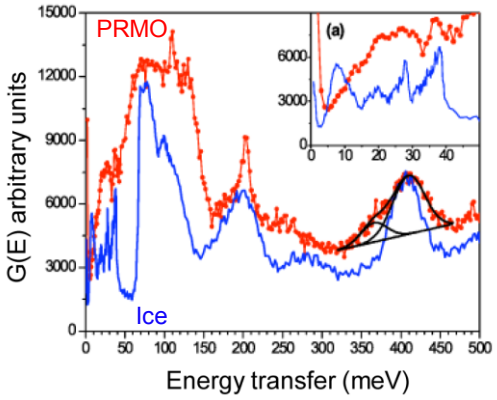

*Fig. 3. INS spectrum for the protonated nanometer sized ramsdellite (PRMO); Dynamics of protons on the surface of the PRMO, with generalized vibrational density of states of protons in the PRMO (top curve with points) as measured by HRMECS spectrometer with E_i=60, 280 at 600 meV. The spectrum of hexagonal ice-Ih (bottom curve, E_i=50, 140 and 600 meV) is shown for comparison. Insert **(a)** shows the energy enlarged translational part of the vibrational spectra.*

We thought that the protons, which have the very weak covalent bonding with oxygen atoms on the surface of PRMO, gave the ability of easy proton conduction in the wet electrolyte for the H_2 sensor application [1]. The network in the orthorhombic crystal structure of ramsdellite [2] is constructed by the short distanced O-O pairs along the b axis shown in Fig. 4. The distances in the O-O pairs are 2.589 and 2.573 Å. We propose that protons conduct in the PRMO particle surface along the network. Studies in the past stated that proton in the ramsdellite prefers the pyramidal oxygen to the planar coordinated oxygen as that site is farther away from the manganese cations, and proton diffuses in the tunnel constructed by MnO_6 octahedra along the b axis of the orthorhombic crystal structure [7]. Regarding lambda-type MnO_2, which contained O-O pairs of interest in its ideal crystal structure, the six O-O pairs make oxygen tetrahedrons distributed independently in the spinel crystal structure. And the protonated lambda-MnO_2 *i.e.*, HMn_2O_4 [8] used in the H_2 sensor, revealed localized O-H vibrations at 113 meV (bending modes) and

416 meV (stretch modes) [9,10]. We expect that these O-H vibrations at 113 meV (bending modes) and 416 meV (stretch modes) are originated from protons in the oxygen tetrahedrons. We thought that the reason why the protonated lambda-MnO_2 showed the higher residual voltage compared to that of the PRMO after pursing H_2 from the sensor [1], probably due to the absence of the oxygen network existing on the surface of the PRMO.

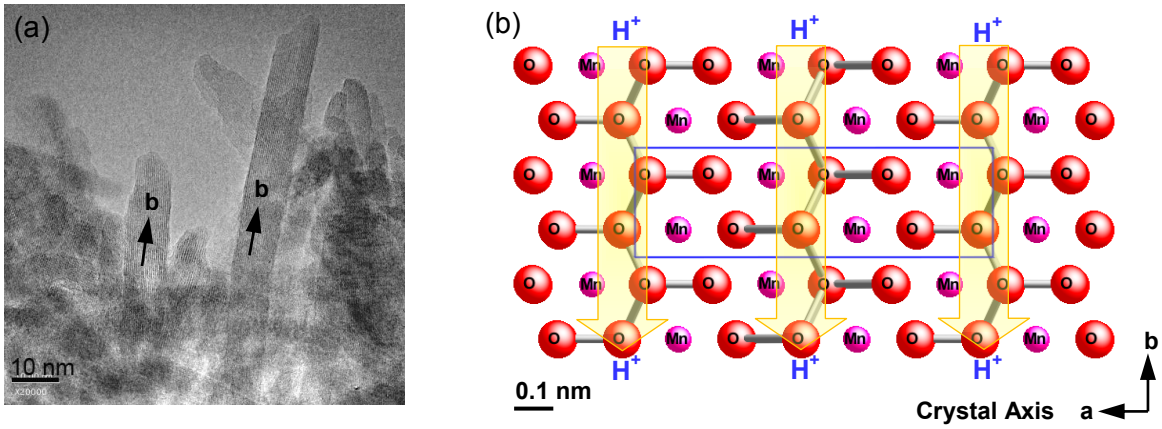

Fig. 4. (a) TEM image of particles and needles of nano-ramsdellite crystal type of MnO_2 (RMO) growing in the direction along the crystal b axis. (b) Schematic illustration of proton conduction routes on the surface of ideal ramsdellite crystal type of MnO_2 [2]. Networks connected by O-O pairs, which have atomic distances of 2.589 Å in the b-axis direction and 2.573 Å in the a-axis direction of the crystal structure of ramsdellite, and proton conduction routes along the networks shown with yellow arrows were illustrated. The blue rectangle drawn at the center of the illustration indicates the unit cell of the crystal structure.

Conclusion

In this study, we propose that a network of oxygen pairs in the ramsdellite-type manganese dioxide enables the best response and residual voltage to H_2 supplied in a hydrogen sensor system due to the good proton conduction. This network model contributes to understand the unique proton conductivity of the manganese dioxide and the operation mechanism of the hydrogen sensor.

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