

## DISCUSSION ON ELECTRODE REACTION IN PARTIAL EQUILIBRIUM STATE BY EMF MEASUREMENTS

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Nanocrystalline porous oxides and hydroxides are known to exhibit high proton and hydroxyl-ion conductivity in wet atmospheres. After a substantial number of challenges to improve the conductivity, it is well established that the surface protonic conduction is related to the hierarchical adsorbed water layer and the proton activity on the surface. However, details of electrode reaction for protonic conduction, which can be alternatively interpreted as a connection of ion formed by an electrode reaction to an ionic bridge, has never been discussed in previous studies. Recently, Stub et al. have measured the emf of the following water vapor concentration cell, Ag |porous-YSZ |Ag, under small water vapor gradients at a constant oxygen pressure, suggesting that the charge carrier is  $\text{H}_3\text{O}^+$  in higher relative humidity ( $\text{RH} > 0.6$ ) and a single proton hopping migration at lower RH region<sup>[1]</sup>. In their work, they assumed that two electrode reactions for  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  shown in the following equilibria, are reversible even at low temperature around room temperature.

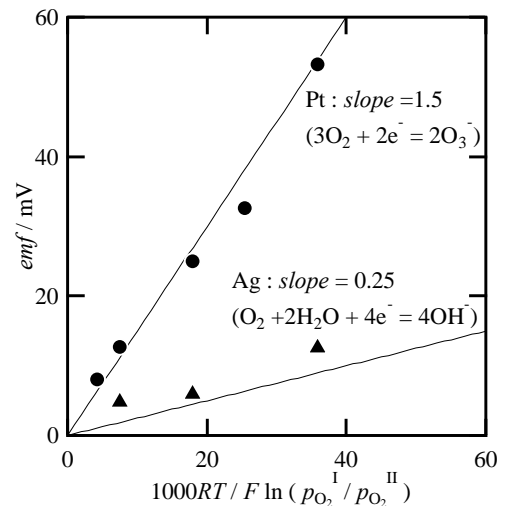


Inspired by their work, we carried out a series of experiments, to understand the relation between the electrode reaction and the emf of concentration cell; how the ion produced by the electrode reaction is connected to the ion migration process in the electrolyte. We employed both emf and AC impedance measurements to discuss the relationship between the electrode reaction and the charge carrier species. The values of emf was measured under a chemical potential gradients of oxygen, hydrogen or water vapor using compacted layered double hydroxide (LDH) as the electrolyte with Pt or Ag electrodes deposited on both sides of the samples by RF magnetron sputter.

Our emf measurements in hydrogen atmosphere suggest that the electrode reaction on Pt electrode,



is reversible because of fast hydrogen dissociation. Also, the H-D isotope effect is clearly observed in AC impedance measurements, indicating single proton hopping is the microscopic rate-limiting step in the ion transport process for macroscopic  $\text{OH}^-$  migration. Therefore, it is concluded that the  $\text{OH}^-$  produced by Eq. (3) eventually transports by the microscopic proton transfer from  $\text{H}_2\text{O}$  molecule to  $\text{OH}^-$ , as suggested theoretically in the previous report<sup>[2]</sup>. In oxidizing atmospheres, however, the emf value of oxygen concentration cell with Pt electrode is extraordinarily larger than the one with Ag electrode, as shown in *Figure 1*. The results suggest that oxygen molecule in the gas phase is apparently reduced to ozonide anion,  $\text{O}_3^-$  on Pt electrode rather than other common oxygen species, such as  $\text{O}^{2-}$ . From the H-D isotope effect estimated by an AC impedance in oxidizing atmosphere, the proton hopping transport on the surface of LDH is confirmed similarly to the one in reducing atmosphere. The extraordinary emf for Pt electrode is possibly due to slow ionic reactions between reduced oxygen inter-mediate on Pt electrode and protonic species on the basic surface of LDH owing to low availability of protonic carriers in the electrolyte. Further details on the relationship between the electrode reaction in the partial equilibrium state and the charge carrier species for various systems will be discussed at the presentation.



*Figure 1* EMF of oxygen concentration cell as a function of the oxygen partial pressure ratio. The slope reflects a reciprocal number of electrons per oxygen molecule in the reversible electrode reaction.

### REFERENCES

- [1] S. Ø. Stub et al. J. Phys. Chem. C, 121, 12817 (2017).
- [2] M. E. Tuckerman et al. Nature, 417, 925 (2002).