DOCTORAL THESIS

Proton conductivity of solid acid RbH_2PO_4 and its composites

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Proton Conductivity of Solid Acid RbH_2PO_4 and its Composites

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Abstract

In this work, RbH_2PO_4 and its composites have been investigated in depth to allow the engineering of these materials with the desired properties for the application in fuel cells. The detailed research progress can be separated into two parts.

In part A, the thermal and electrical properties of pure RbH_2PO_4 are first studied. In the heating process, two thermal events take place at $T_p \approx 109$ °C and $T_p' \approx 276$ °C, respectively. The former is confirmed to be a structural transition from tetragonal phase (III) to monoclinic phase (II). The latter is also viewed as a potential phase transition from II to an as-of-yet unidentified phase (I). The difficulty of the confirmation of second phase transition arises from the interference of high-temperature (HT) decomposition of RbH_2PO_4. Other thermal behaviors are entirely attributable to dehydration. In order to suppress this dehydration/decomposition and keep complete structures of RbH_2PO_4, highly humidified N_2 atmosphere with water partial pressure at $P_{H_2O} \approx 0.56$ atm is used. Under such conditions, the proton conductivity of RbH_2PO_4 is measured. With increasing temperature, the conductivity rises smoothly at T_p and then jumps by about two orders of magnitude at T_p' to the level of 10^{-2} S/cm finally. This result indicates a superprotonic phase transition nature. Thus RbH_2PO_4 belongs to superprotonic conductor, similar to CsH_2PO_4 and $CsHSO_4$.

Despite the fact that RbH_2PO_4 exhibits high proton conductivity at HT (> T_p'), it still can not satisfy the requirement of practical applications because its low-temperature (LT) conductivity is too low. This limits the operating temperature of such a fuel cell with RbH_2PO_4 as electrolytes only above ~276 °C. To widen the temperature range, the

LT conductivity of RbH_2PO_4 needs to be strongly enhanced by eliminating the superprotonic phase transition.

In part B, heterogeneous doping method is employed and RbH_2PO_4-based composites with SiO_2 particles as dopants are studied. It is found that the LT conductivity of RbH_2PO_4/SiO_2 composites has been enhanced, which relies on the amount of dopants. The optimum molar fraction of SiO_2 is between ~0.45 and ~0.65. Various reasons for the conductivity enhancement in composites have been considered. The possible influence of adsorbed water on SiO_2 particles on enhanced conductivity is eliminated. Via a series of experimental characterizations, a new interface phase, i.e., amorphous RbH_2PO_4, is confirmed to form during mechanical milling and sintering treatment. This amorphous phase leads to the fast proton conduction and high conductivity even at LT.

The present work suggests RbH_2PO_4-based composites can serve as electrolyte candidate in future solid acid fuel cells (SAFCs).

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