DOCTORAL THESIS

# Proton conductivity of solid acid $RbH_2PO_4$ and its composites

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*Date of Award:*
2012

# Proton Conductivity of Solid Acid $RbH_2PO_4$ and its Composites

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A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

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Hong Kong Baptist University

December 2011

# 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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