

HIGH CAPACITY BATTERY ELECTRODE MATERIAL OBTAINED BY THE STABILIZATION OF MAGNESIUM HYDRIDE IN THE FLUORITE STRUCTURE

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Recently the new lightweight NiMH battery electrode material magnesium scandium hydride was reported to have a much higher capacity than standard LaNi₅-type electrode materials [1]. For the composition Mg_{0.65}Sc_{0.35}Pd_{0.024}H_x more than 1000 mAh/g of charge can be extracted at a 50 mA/g rate. The magnesium content of these electrode materials can be between 50 and 80 mole percent, combining the low specific weight of magnesium hydride with the good kinetic properties of the fluorite structure. The material was discovered as a spin-off from research on metal hydrides with optical properties dependent on the hydrogen content [2]. These optically switchable materials are ionic in the hydrogen-filled state. The structure of scandium magnesium hydride has been studied as a function of scandium content. X-ray diffraction measurements show the structure to be cubic for a large scandium concentration range. Analogous to scandium di-hydride the XRD pattern of the hydrogen saturated compositions fit a simulation of a fluorite structure.

In the fluorite structure the cations form a fcc structure with the anions filling all the tetrahedral positions in the unit cell. All large octahedral sites remain empty. If in fluorite structured CaF₂ part of the divalent calcium is substituted for trivalent yttrium, the charge compensating fluoride ions will fill these octahedral sites. The ionic conductivity increases by orders of magnitude due to these highly mobile interstitial fluoride ions [3]. Due to the chemical similarity between negatively charged hydrogen and fluoride ions hydrides and fluorides often show similar behavior [4]. Indeed the material YbH_{2.55} has been reported to have a very high ionic conductivity [5]. This material contains a mixture of divalent and trivalent ytterbium.

In order to improve the hydrogen mobility in magnesium hydride it has been successfully attempted to stabilize magnesium di-hydride in the fluorite structure by partially substituting the magnesium with trivalent scandium.

Interstitial hydrogen ions would then be highly mobile in the large empty octahedral sites of the structure.

Comparing the extracted charge at 50 mA/g of fully hydrogenated Mg_{0.65}Sc_{0.35}Pd_{0.024}H_x (1008 mAh/g) with that of fully hydrogenated MgPd_{0.024}H_x (8 mAh/g) it can be concluded that the discharge kinetics of the fluorite-structured hydride is much better than that of the rutile-structured magnesium hydride containing the same amount of palladium.

Chemical analysis as well as coulometry determine the hydrogen content of fully hydrogenated Mg_{0.65}Sc_{0.35}Pd_{0.024}H_x to be more than 2.2 hydrogen per metal atom. This is in agreement with a charge compensating role of the negatively charged hydrogen for the substitution of divalent magnesium by trivalent scandium.

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