Zinc–air batteries offer the potential of low-cost energy storage with high specific energy, but at present secondary Zn–air batteries suffer from poor cyclability. To develop economically viable secondary Zn–air batteries, several properties need to be improved: choking of the cathode, catalyzing the oxygen evolution and reduction reactions, limiting dendrite formation and suppressing the hydrogen evolution reaction (HER). Understanding and alleviating HER at the negative electrode in a secondary Zn–air battery is a substantial challenge, for which it is necessary to combine computational and experimental research. Here, we combine differential electrochemical mass spectrometry (DEMS) and density functional theory (DFT) calculations to investigate the fundamental role and stability when cycling in the presence of selected beneficial additives, that is, In and Bi, and Ag as a potentially unfavorable additive. We show that both In and Bi have the desired property for a secondary battery, that is, upon recharging they will remain on the surface, thereby retaining the beneficial effects on Zn dissolution and suppression of HER. This is confirmed by DEMS, where it is observed that In reduces HER and Bi affects the discharge potential beneficially compared to a battery without additives. Using a simple procedure based on adsorption energies calculated with DFT, it is found that Ag suppresses OH adsorption, but, unlike In and Bi, it does not hinder HER. Finally, it is shown that mixing In and Bi is beneficial compared to the additives by themselves as it improves the electrochemical performance and cyclic stability of the secondary Zn–air battery.