

## Electronic Supplementary Information

### Combining catalysis and hydrogen storage in direct borohydride fuel cells: towards more efficient energy utilization

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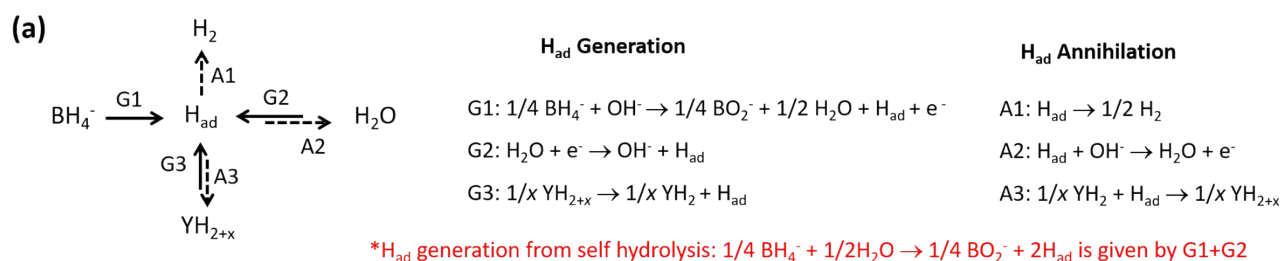
#### Potential dependent H chemical potential of different H species:

#### Derivation and discussions

##### 1. Definition and general expression for the H chemical potential

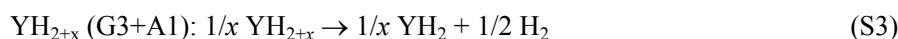
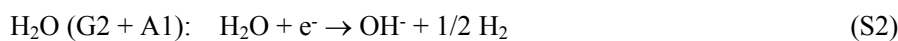
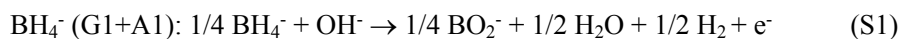
The energy of H in hydrogen storage materials can be described by the equilibrium  $H_2$  partial pressure, or equivalently, the chemical potential of  $H_2$  in the equilibrium state. The chemical potential of  $H_2$  in the equilibrium state (H chemical potential,  $\mu_H$ ) can be extended as a general descriptor to measure the energy of H in H species, including solids, liquids and solution species. The H species for investigation is in the standard state, i.e. pure substance for solids or liquids and concentration of 1 M for solution species. For  $H_2$  in the standard potential, i.e. partial pressure is  $p^0$  (1 bar),  $\mu_H = 0$ .

We will calculate the H chemical potential  $\mu_H$  of  $BH_4^-$ ,  $YH_{2+x}$  and  $H_2O$  in the  $NaBH_4$ - $YH_{2+x}$ - $H_2O$  system, corresponding to the hydridic, atomic and protonic H. The interconversion reactions of the H species are shown in Figure S1 (same as Figure 4a in the main text). Here G1 is given by the average of oxidative dissociation of the four B-H bonds in  $BH_4^-$ .



**Figure S1.** Interconversion reactions of the H species in the  $NaBH_4$ - $YH_{2+x}$ - $H_2O$  system

For calculation, the first step is to correlate the H species with H<sub>2</sub>. This can be readily done by coupling the three H<sub>ad</sub> generation reactions (G1, G2 and G3) with the H<sub>2</sub> formation reaction (A1):



Note that the coefficient of the reactions are adjusted to given 1 mol H atom in H<sub>2</sub>, i.e. 1/2 mol H<sub>2</sub>.

The equilibrium chemical potential of H<sub>2</sub> is related to the equilibrium H<sub>2</sub> partial pressure  $p_{\text{H}_2}^{eq}$ :

$$\mu_{\text{H}} = 1/2 RT \ln(p_{\text{H}_2}^{eq}/p^0) \quad (\text{S4})$$

Here  $p^0 = 1$  bar is the pressure at the standard state,  $R=8.314$  J·mol<sup>-1</sup>·K<sup>-1</sup> is the ideal gas constant and  $T$  is the temperature in Kelvin.

When all the solution species is in the standard state, i.e. concentration is 1 M, the Gibbs free energy change of the reactions (S1, S2 and S3)  $\Delta G_i$  ( $i = 1-3$ ) is only affected by the H<sub>2</sub> partial pressure, which is given by:

$$\Delta G_i = \Delta G_i^0 + 1/2 RT \ln(p_{\text{H}_2}^{eq}/p^0) \quad (\text{S5})$$

Here  $\Delta G_i^0$  is the standard Gibbs free energy change of the corresponding reaction.

$\Delta G_i$  can also be given by the electrode potential  $\varphi$  through:

$$\Delta G_i = -nF\varphi \quad (\text{S6})$$

Here  $F=96480$  C·mol<sup>-1</sup> is the Faraday constant,  $n$  is the number of electrons required to generate 1 mol H in H<sub>2</sub> (or equivalently 0.5 mol H<sub>2</sub>).

Combining S4, S5 and S6, we can obtain the general expression for  $\mu_{\text{H}}$ :

$$\mu_{\text{H}} = -\Delta G_i^0 - nF\varphi \quad (\text{S7})$$

The possible values for  $n$  to generate 1 mol H is +1, -1 or 0. If H<sub>2</sub> is generated through a reductive reaction (i.e. water reduction, Eq. S2), then  $n = 1$ . If H<sub>2</sub> is generated through an oxidative reaction (i.e., BOR, Eq. S1), then  $n = -1$ . If H<sub>2</sub> is generated through a non-redox reaction (i.e. dehydrogenation of YH<sub>2+x</sub>, Eq. S3), then  $n = 0$ . For redox reactions, Eq. S7 is equivalent to the Nernst's Equation. Using the above assignment of the  $n$  value, the non-redox reaction can also be included.

Therefore,  $\mu_{\text{H}}$  can be calculated from the standard Gibbs free energy change  $\Delta G_i^0$  ( $i = 1-3$ ).

## 2. $\mu_H$ in different H species

### 2.1 $\mu_H$ in $H_2O$

The corresponding  $H_2$  generation reaction is Eq.S2, which is the  $H_2$  evolution reaction from  $H_2O$  in alkaline solution. The standard potential of the  $H_2O/H_2$  redox couple is the reversible hydrogen electrode potential (RHE, -0.83 V vs. SHE) in 1 M  $OH^-$ . Thus,

$$\Delta G_2^o = -F\varphi_{RHE}^o \quad (S8)$$

Substitute Eq. S8 into Eq. S7 and note here  $n = 1$ , we obtain:

$$\mu_H(H_2O) = -\Delta G_2^o - nF\varphi = F\varphi_{RHE}^o - F\varphi \quad (S9)$$

Using eV as the unit leads to a simpler expression:

$$\mu_H(H_2O) = -\varphi + \varphi_{RHE}^o \quad (S9a)$$

### 2.2 $\mu_H$ in $NaBH_4$

The corresponding  $H_2$  generation reaction from  $BH_4^-$  is Eq.S1. To calculate  $\Delta G_1^o$ , we note that the combination  $4(S2 - S1)$  gives the borohydride oxidation reaction (BOR, Eq. S10):



Thus, the  $\Delta G^o$  of S10 is given by:

$$\Delta G_{10}^o = 4\Delta G_2^o - 4\Delta G_1^o = -8F\varphi_{BOR}^o \quad (S11)$$

Here  $\varphi_{BOR}^o = -1.24$  V vs SHE is the standard potential for the  $BO_2^-/BH_4^-$  redox couple.

Combine Eq. S8, S11 into Eq. S7 and note here  $n = -1$ ,  $\mu_H$  in  $NaBH_4$  is given by Eq. S12:

$$\begin{aligned} \mu_H(NaBH_4) &= -\Delta G_1^o + F\varphi = -(\Delta G_2^o + 2F\varphi_{BOR}^o) + F\varphi \\ &= F\varphi_{RHE}^o - 2F\varphi_{BOR}^o + F\varphi \end{aligned} \quad (S12)$$

Using eV as the unit leads to a simpler expression:

$$\mu_H(NaBH_4) = \varphi + \varphi_{RHE}^o - 2\varphi_{BOR}^o \quad (S12a)$$

### 2.3 $\mu_H$ in $YH_{2+x}$

The corresponding  $H_2$  generation reaction is Eq. S3. The  $\Delta G^o$  of S3 is given by

$$\Delta G_3^o = \Delta G_{deH}^o \quad (S13)$$

Here  $\Delta G_{deH}^o$  is the Gibbs free energy change of the standard dehydrogenation process. Therefore,  $\mu_H$  in  $YH_{2+x}$  is simply given by (here  $n = 0$ ):

$$\mu_H(YH_{2+x}) = -\Delta G_{deH}^o \quad (S14)$$

For  $YH_{2+x}$  to  $YH_2$ , the dehydrogenation enthalpy at 298 K  $\Delta G_{deH}^o$  at 298 K is 31 kJ·(mol H)<sup>-1</sup>, obtained from the van't Hoff isotherm<sup>1</sup>. The entropy of H<sub>2</sub> is 130.8 J mol<sup>-1</sup> K<sup>-1</sup>.<sup>2</sup> Therefore,  $\Delta G_{deH}^o$  at 298 K is calculated to be 11.5 kJ·(mol H)<sup>-1</sup>, or 0.12 eV.

### 3. Summary and plot

The H chemical potential (in eV) of different H containing species shows very simple linear dependence on the electrode potential  $\varphi$ , which is summarized as:

$$\mu_H(H_2O) = -\varphi + \varphi_{RHE}^o \quad (S9a)$$

$$\mu_H(NaBH_4) = \varphi + \varphi_{RHE}^o - 2\varphi_{BOR}^o \quad (S12a)$$

$$\mu_H(YH_{2+x}) = \Delta G_5^o - \Delta G_3^o = -\Delta G_{deH}^o \quad (S14)$$

Using  $\varphi_{RHE} = -0.83$  eV,  $\varphi_{BOR}^o = -1.24$  eV and  $-\Delta G_{deH}^o = 0.12$  eV, the  $\mu_H \sim \varphi$  plot is shown in Figure S2 (similar to Figure 5 in the main text). At a given electrode potential, lower  $\mu_H$  species is more stable. We can check the correctness of the above equations by comparing them with physical definition. Calculated from Eq. S9a and Eq. 12a, the intercepts of the  $BH_4^-/H_2O$  line gives  $\varphi = \varphi_{BOR}^o$ , indicating  $BH_4^-$  can only be oxidized into H<sub>2</sub>O above that potential, which is in perfect agreement with the physical definition of  $\varphi_{BOR}^o$ .

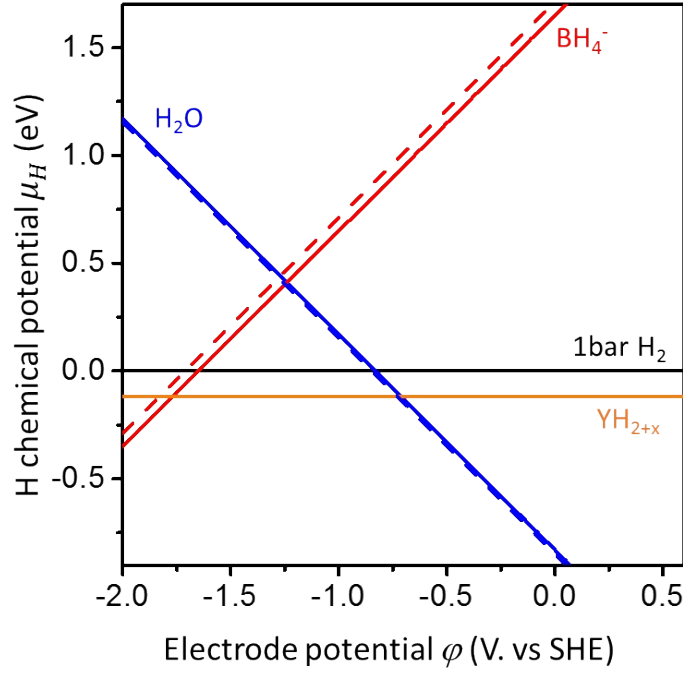


Figure S2 The potential dependent H chemical potential of different H containing species. The solid lines are corresponding to the standard condition, i.e. the concentration of all the solution species is 1 M. The dashed lines are results after correction for the non-standard concentration:  $[\text{OH}^-] = 2 \text{ M}$ ,  $[\text{BO}_2^-]/[\text{BH}_4^-] = 10^{-3}$ .

#### 4. Correction for the non-standard concentration

Eq. S9a and Eq. S12a are derived for the standard condition, i.e. the concentration of  $\text{BH}_4^-$ ,  $\text{BO}_2^-$  and  $\text{OH}^-$  is 1 M. However, the  $\text{NaBH}_4$  and  $\text{NaOH}$  concentration are 0.05 M and 2 M in the experiment. The concentration of  $\text{BO}_2^-$  is unknown. The electrode potential for reaction S2 and S10 should be corrected for the non-standard concentration. This can be done by applying the Nernst equation for reaction S2 and S10.

$$\varphi'_{RHE} = \varphi^o_{RHE} + 0.0592 \log \frac{1}{[\text{OH}^-]} \quad (\text{S15})$$

$$\varphi'_{BOR} = \varphi^o_{BOR} + \frac{0.0592}{8} \log \frac{[\text{BO}_2^-]}{[\text{BH}_4^-][\text{OH}^-]^8} \quad (\text{S16})$$

The experimental concentration for  $\text{OH}^-$  is 2 M.  $[\text{BO}_2^-]/[\text{BH}_4^-]$  is unknown but  $10^{-3}$  is a reasonable value. Substitute into the above equations give:

$$\varphi'_{RHE} = \varphi^o_{RHE} - 0.018 \quad (\text{S17})$$

$$\varphi'_{BOR} = \varphi^o_{BOR} - 0.040 \quad (\text{S18})$$

Therefore, the  $\varphi_{RHE}^{\circ}$  and  $\varphi_{BOR}^{\circ}$  in Eq. S9a and S12a should be replaced by  $\varphi_{RHE}^{\prime}$  and  $\varphi_{BOR}^{\prime}$  for non-standard concentration. Thus, the non-standard concentration only cause very slight shift of  $\mu_H$ , which is shown by the dashed lines in Figure S2. The concentration effect on  $\mu_H$  is rather insignificant.

## References

1. R. Griessen, J. N. Huiberts, M. Kremers, A. T. M. van Gogh, N. J. Koeman, J. P. Dekker and P. H. L. Notten, *Journal of Alloys and Compounds*, 1997, **253–254**, 44-50.
2. L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353-358.