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## **‘Hydrogen storage’ under oxidative conditions: a pandemic case**

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### **Abstract**

This Opinion attracts attention to an evident problem with interpretation of some data for oxides and oxide-based compositions in aqueous alkaline medium in terms of ‘hydrogen storage’. The potentials corresponding to both ‘charge’ and ‘discharge’, as reported in numerous recently published works, exceed oxygen equilibrium potential. Under these highly oxidative conditions, the risk of by-side processes is high enough. The reported record values of ‘discharge capacity’ can be hardly agreed with any possible type of hydrogen bonding in oxide lattice.

**Keywords:** Electrochemical hydrogen storage; Oxides; Coulometry; Charge; Discharge

### **What is electrochemical hydrogen storage?**

Hydrogen storage (HS) in condensed state without application of low temperatures and high H<sub>2</sub> pressure is an important part of ‘hydrogen economy/energy’ concepts, which intensified again in the last decade. HS systems [1] support two general types of the processes with participation of either molecular or atomic hydrogen: hydrogen bonding (in solid or liquid bulk, or at the interface), and hydrogen extraction.

Electrochemical HS (EHS) occupies an important, but a limited space in the area [2]. Two most general EHS strategies are reversible sorption/desorption and conversion (typical for organic hydrogen carriers [3, 4]). In what follows only sorption strategy is considered. It assumes hydrogen bonding in some matrix by means of H<sup>+</sup> or H<sub>2</sub>O reduction to form H atoms and/or H<sub>2</sub> molecules (*cathodic process, charge*) and oxidation of H or H<sub>2</sub> to H<sup>+</sup> (*anodic process, discharge*). These processes are sometimes named ‘electrosorption’. Charge and discharge occur more or less reversibly for the most studied 3D matrices hosting hydrogen *in the bulk*, like intermetallics [5, 6] or high entropy alloys [7]. Another possibility is ‘2D EHS’ in highly dispersed materials [8] hosting H<sub>2</sub> or hydrogen adatoms H<sub>ad</sub> as a (sub)monolayer *at the surface*. Considering gas-phase HS vs. EHS [9], one can articulate the following points.

1. As the nature of hydrogen bonding in the bulk is the same for each matrix, equilibrium features of both gas-phase and electrochemical processes are also the same. *Equilibrium hydrogen/matrix ratios* are equal at a given hydrogen pressure and at potential corresponding to this pressure according to Nernst Equation for H<sub>2</sub>O/H<sub>2</sub>.
2. In case of bonding to the matrix surface, a certain difference can be observed for *equilibrium surface coverage* in the gas-phase and in electrochemical systems, resulting from co-adsorption of electrolyte components. However for relatively strong hydrogen bonding this difference is minor.
3. Assuming pH dependence of H<sub>2</sub>O/H<sub>2</sub> equilibrium potential, all EHS processes are regulated by potential in the scale of the reversible hydrogen electrode (RHE), not in pH-independent scale. *This point is misunderstood dramatically in the literature, see below.*

4. ‘Dry’ (gas-phase) and ‘wet’ (EHS) processes can demonstrate some kinetic difference, especially if interfacial steps are slow. If sorption-desorption of hydrogen into 3D matrices (intercalation) is limited by diffusion in the solid state, the observed reaction rate is not affected by external medium. In this case no difference is expected even in the absence of equilibrium.
5. HS capacity cannot be unlimited. For 3D case, the capacity is determined by the stoichiometry of *bulk* hydrides or other compounds formed in the matrix. For 2D, the capacity is typically limited to monolayer of hydrogen adsorbate.
6. Coulometry is typically applied to quantification of the hydrogen/matrix ratio. To assigned measured charge unambiguously, one needs to exclude the processes not related to hydrogen, which means to understand first the nature of hydrogen bonding. Being well understood for many traditional matrices [9], bonding nature requires clarification for new HS materials.

Recent reviews on EHS [10, 11] mention various complex compounds, in particular, metal oxides. For ‘dry’ HS by oxides, the conversion-type processes are known: H<sub>2</sub> reduces oxide to metal, and metal is oxidized by H<sub>2</sub>O [12-14]. Conversion is reversible only at high temperature, excluding the direct electrochemical analogy. Sorption-type EHS by non-stoichiometric oxides presents the proton-coupled electron transfer [15]. Molecular or atomic hydrogen with zero oxidation state is not involved, so more correct definition for these redox transformations accompanied by proton intercalation/deintercalation is “*hydrogen ion storage*”. It is possible for transition metal oxides (and probably for tin oxide), but not for Zn- and Al-oxides mentioned in Ref. 10. *This type of storage can be hardly considered for hydrogen as a fuel*, but can be probably of interest for more particular applications.

### **The opposite is true? Cathodic “discharge” and anodic “charge” above equilibrium oxygen potential**

The author of this Opinion studied about two dozen of ‘EHS by oxides’ articles. The total number of the articles of a similar structure (mostly published by several mutually linked groups) is evidently higher. The choice of example considered below [16] is justified by publication in *Electrochimica Acta*. Actually, penetration of improperly arranged works into specialized journal (hopefully occasional) presents even more serious trouble than numerous publications in material science related journals. The author’s motivation is to enhance electrochemical expertise.

Ref. 16 presents the data for Mo-based complex oxides (formulas in Fig. 1a) and starts from the statement about oxide redox transformations, which can be understood like “hydrogen ion storage” mentioned above. Further mentioned pathway is explained as follows: ‘...working electrode material (M) is charged by the electrochemical absorption of hydrogen and the electrochemical evolution of hydroxyl ion Eq. (3);  $M + H_2O + e^- \rightarrow M-H + HO^-$  (3), and discharged in order to form water and electron Eq. (4):  $M-H + ^-OH \rightarrow M + H_2O + e^-$  (4)’. The proposed scheme (3)-(4) does not assume any M redox transformation, but still corresponds to cathodic charge and anodic discharge. Then the authors show the voltammogram (Fig. 1a) measured at pH 7 in K<sub>3</sub>(Fe(CN)<sub>6</sub>)/K<sub>4</sub>(Fe(CN)<sub>6</sub>) (Experimental). The formal potential for quasi-reversible redox feature is close to equilibrium value for (Fe(CN)<sub>6</sub>)<sup>3-/4-</sup> couple (slightly shifted, probably because of ion pairing) and has no any relation to oxide redox behavior. What is really seen for oxide (consider the potentials in RHE scale, blue axis below the plot in Fig. 1a) is the cathodic ‘tail’, presumably the irreversible Mo(VI) reduction, which is not discussed by the authors.

Galvanostatic experiment in 6 M KOH is presented in Ref. 16 as ‘discharge’ (Fig. 1b), which is anodic process. However, the subsequent transients demonstrate potential decrease typical for cathodic process (in contradiction with the pathway cited above). This ‘discharge’ occurs near the upper boundary of electrolyte stability region (dashed blue line). For the ‘charge’ (inset), potential increases with time, which means anodic polarization. ‘Charge’ potentials already correspond to hundreds mV oxygen overvoltage (red axis near the inset), exceeding peroxide/water and approaching ozone/water equilibrium potentials. 20 cycles of so sharp oxidation and subsequent reduction result in increase of ‘discharge capacity’ up to 3250 mAh/g.

For  $\text{SrCe}_{1.6}(\text{MoO}_4)_4\text{Ho}_{0.1}\text{Yb}_{0.3}$  (molecular mass >1000, 1 g is < 0.001 mole) the reported ‘capacity’ corresponds to  $3250 \times 3.6 \text{ C/F} \sim 0.12$  equivalents, or  $\sim 0.12/0.001 = 120$  electrons per formula unit, four times higher than for complete reduction of oxide to metals. This surprisingly high value can only result from the charge spent for some by-side processes. To say, horizontal ‘charge’ plateaus (Fig 1b, inset) may correspond to oxygen-related faradaic reactions, namely oxygen evolution from water and from oxide lattice [17]. There are no doubts that oxide can undergo various transformations at so high potentials, to say, oxygen stoichiometry increase [18] and irreversible destruction. The anodic ‘charging’ under these circumstances can result in accumulation of oxidation products in solution, so it is not surprising that cathodic ‘discharge’ demonstrates the ‘capacities’ increasing with cycle number. The dramatic hysteresis of ‘charge’ and ‘discharge’ (hundreds of mV) demonstrates the pronounced irreversibility.

Earlier article [19] on the EHS in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  was also noticed in *Electrochimica Acta*, with a Figure reproduced later in review [11]. ‘Charge’ [19] is indicated for increasing potential transients with horizontal plateau at ca. +1.4 V vs.  $\text{NiOOH}/\text{Ni}(\text{OH})_2$ , already far above equilibrium oxygen potential. It is difficult to investigate who was the first to announce this behavior under highly oxidative conditions as EHS and who started to use charge-discharge notions, but the number of the followers is increasing rapidly.

In the majority of other articles on ‘EHS by oxides’ the transients for ‘charge’ are simply absent, only descending ‘discharge’ in the vicinity of oxygen potential is shown. Usually reported EHS scheme is ‘oxide +  $\text{gH}_2\text{O} + \text{ge}^- \Leftrightarrow (\text{gH}+\text{oxide}) + \text{gHO}^-$ ’. This uncertain designation ( $\text{gH}+\text{oxide}$ ) is discussed in terms of either absorption or adsorption. When the ‘capacities’ of thousands of mAh/g are reported, coefficient g appears to be of the order of dozens per formula unit. So high number of hydrogen atoms per oxide unit cannot be combined with any realistic consideration of bonding in the bulk. Interfacial bonding is mostly announced for highly dispersed materials.

### **Adsorption/spillover in ‘hydrogen sorption by oxides’ context: one more turn?**

Let us consider an example [20] for  $\text{ZrO}_2$  supported by graphene oxide (GO), with 390  $\text{m}^2/\text{g}$  specific surface area (BET). Assuming more modest ‘discharge capacity’ of 320 mAh/g [20], the specific charge per real surface area can be estimated as  $\sim 0.3 \text{ mC}/\text{cm}^2$ , which is basically possible for a monolayer. (Note that GO is just an example of ‘hydrogen ion sorption’ material. It undergoes proton-coupled redox transformations of the interfacial oxygen-containing groups which occupy 30-40% of the surface and may require more than one electron for transformations [21]).

The data presented in Ref. [20] allow one to compare the voltammograms and galvanostatic curves in the same alkaline solution (Fig.2). The former (Fig. 2a) are measured in extremely wide potential interval, but the observed redox feature II (more or less reversible) corresponds to the region of electrolyte stability. The authors’ assignment of II ( $\sim +0.5 \text{ V RHE}$ ) to hydrogen

evolution cannot be accepted, as hydrogen gas can only evolve below zero potential in RHE scale. This feature (corresponding probably to oxide recharging) is absent from galvanostatic curves (Fig. 2b), which start from the region of irreversible cathodic peak *I*. Like in Ref. 16, ‘charge’ is anodic and takes place at very high oxygen overvoltage, just at potentials of anodic ‘tail’ in Fig. 2a. ‘Discharge’ is cathodic, does not correlate with any voltametric features, and is interpreted as hydrogen spillover from ZrO<sub>2</sub> to GO. However dissociative H<sub>2</sub> adsorption discussed by the authors cannot occur on oxide, and no molecular or atomic hydrogen can survive at potentials above +1.1 V RHE (formally, according to Nernst Equation, this corresponds to hydrogen effective pressure below 10<sup>-38</sup> atm).

Few years later *the same authors* reported *the same ZrO<sub>2</sub>/GO system* modified with Ni and Co metals [22], with comparable capacity values of 416 and 291 mAh/g for materials with BET areas of 185 and 100 m<sup>2</sup>/g respectively. For these systems hydrogen spillover is quite usual [23, 24] because H adatoms can be formed on metals and move to oxide and to carbon surfaces. Unexpectedly, in Ref. 22 we see the signs opposite to that presented in Ref.20: cathodic charge and anodic discharge (Fig.3). Both occur at potentials of electrolyte stability. Quasi-reversible voltametric feature *II* in Fig. 3a is the same as in Fig. 2a, being typical for ZrO<sub>2</sub> and providing very low contribution to galvanostatic charging (Fig. 3b). Irreversible peak *III* (absent in Ref. 20, related presumably to hydrogen on metal) corresponds to the major part of charge plateau. Surely H<sub>2</sub> recombination declared in Ref. 22 cannot take place at positive RHE potentials of peak *III*, because the specific charge of 0.7-0.9 mC/cm<sup>2</sup> seems to be too high for monolayer, and other details also require discussion. However, the most impressive is transformation in the authors’ consciousness in respect to EHS.

### Concluding remarks

HS is a wide area containing various branches of debating nature. To provide an example, carbon materials and especially carbon nanomaterials are actively studied in respect to EHS [10, 11, 25]. Simultaneously, gas-phase HS community is rather sceptic in respect to room-temperature sorption of hydrogen by carbon materials [1]. Debates resulted in appearance of important works [26-28] attracting attention to details of sorption experiments. The problem considered above is also related to experimental aspects. Briefly, electrochemical measurements provide the values of charge, but can never assign these values to certain processes automatically. ‘EHS at oxygen evolution potentials’ is just a problem of incorrect assignment.

The only possible way to stop the pandemic spreading of improper assignment is to restrain publication of the articles like considered above as examples. The reviews require special attention. Namely, the review [10] collecting the record capacity values up to 4650 mAh/g and contradictory original works [20, 22] seems to be misleading. The review [11] contains the Figures confusingly presenting ‘charge’ and ‘discharge’ in a normal and inverted way simultaneously. Our most important duty is to check the origin of any reported values and to provide critical analysis, if necessary.

In a widely known interview [29] J.O’M Bockris, one of the most active enthusiasts of the ‘hydrogen economy’, considered ‘hydrogen public image’ as the foremost barrier (associated with thermal explosions and hydrogen bomb). He could hardly predict how the area will develop from electrochemical side (see above). What I worry about now, when new ‘hydrogen energy’ mainstream is submerging various scientific journals, is the quality of our specialized expertise.

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**Declaration of interest:** none

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## Figure Captions

Fig.1. *a* – cyclic voltammogram (Fig. 7 in Ref. 16); according to information in section 2.2, p.2 (absent from Figure 7 caption [16]), the curves are measured in 0.1 M phosphate buffer solution, pH 7, containing K<sub>3</sub>(Fe(CN)<sub>6</sub>)/K<sub>4</sub>(Fe(CN)<sub>6</sub> (concentration is not indicated) with 10 mV/s scan rate; *b* – chronopotentiometric data (Fig. 8c with inset in Ref. 16, presented for SrCe<sub>1.6</sub>(MoO<sub>4</sub>)<sub>4</sub>Ho<sub>0.1</sub>Yb<sub>0.3</sub> material with the highest ‘discharge capacity’ in the series) for subsequent 1...20 ‘charge-discharge’ cycles. All comments in *Italic*, all dashed lines, potentials vs RHE, oxygen overvoltage axis, and the arrows are added by the author of this Opinion. Red arrows demonstrate the starting point of ‘discharge’, which is ca. 0.45 V lower than the starting potential of ‘charge’ (see *b*, inset). RHE zero is calculated assuming the mean activity coefficient of ~2.3 for 6 M KOH at room temperature (pH ~ 15) and AgCl/Ag zero of 0.2 V vs. SHE. The uncertainty is induced by the fact that chloride concentration for AgCl/Ag is not indicated in Ref. 16. As this uncertainty hardly exceeds ~0.05 V, it is not crucial for our general analysis of potential intervals.

Fig.2. *a* - cyclic voltammogram (20 mV/s, Fig. 5 in Ref. 20); *b* – ‘charge-discharge’ curves (2.5 mA/g, Fig.8 in Ref. 20). All comments in *Italic*, all dashed lines, potentials vs RHE, roman numerals, and an arrow (indicates hydrogen evolution assignment of cathodic peak in Ref. 20, pp.21865; 21867) are added by the author of this Opinion. RHE zero is calculated assuming the mean activity coefficient of ~2.3 for 6 M KOH at room temperature (pH ~ 15) and AgCl/Ag zero of 0.2 V vs. SHE. The uncertainty is induced by the fact that chloride concentration for AgCl/Ag is not indicated in Ref.20; moreover, in Experimental calomel reference electrode is indicated (p.21863), also without information on chloride concentration. As this uncertainty does not exceed ~0.05 V, it is not crucial for our general analysis of potential intervals.

Fig.3. *a* - cyclic voltammogram (10 mV/s, Fig. 7A in Ref. 22); *b* – charge-discharge curves (25 mA/g, Fig.7B in Ref. 22). All comments in *Italic*, all dashed lines, potentials vs RHE, and numeral *II* (indicates the same feature as *II* in Fig. 2a) are added by the author of this Opinion. RHE zero corresponds to ~ – 0.93 V HgO/Hg. Pay attention to potential axis opposite direction as compared to Figs 1b and 2b above.

Fig.1

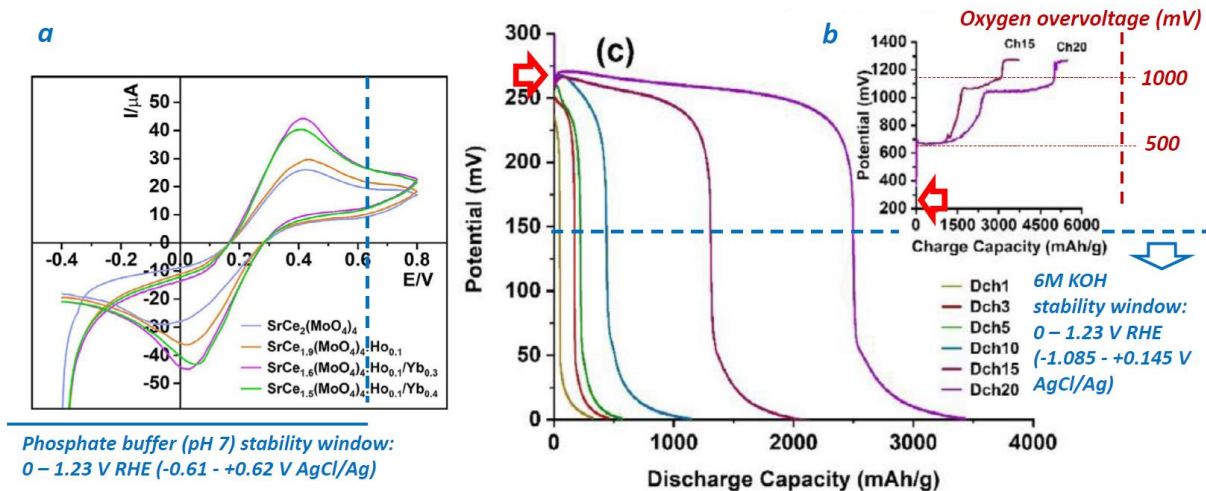


Fig.2

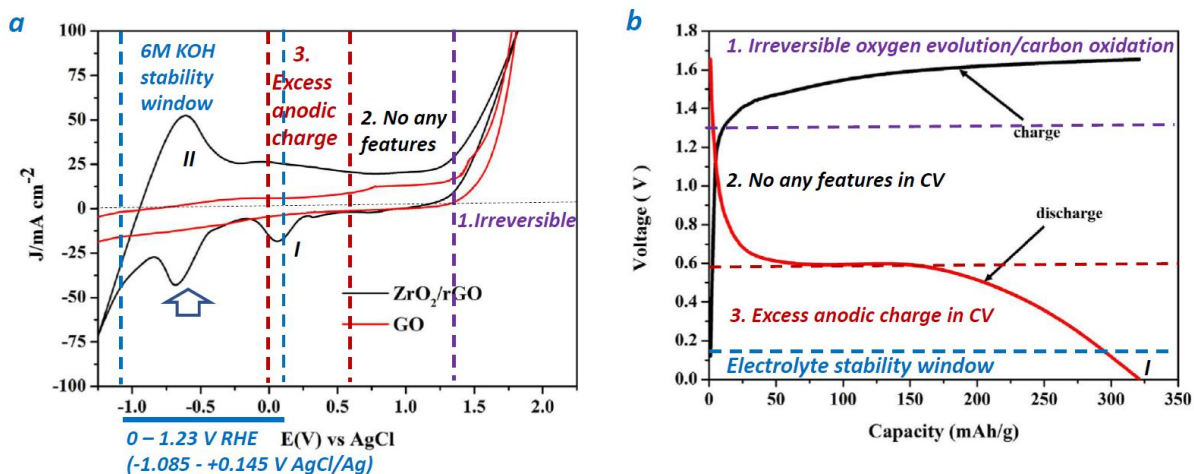


Fig.3

