

On Electrochemical Managing the Properties of Aqueous Coolant

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Abstract

Liquid water as a chemical compound with the wide band gap is characterized by varying their Fermi level as a linear identifier of water oxidation-reduction potential (ORP). This potential is the management tool for changing chemical properties of the aqueous coolant by forced shifting Fermi level in the band gap at the expense of insignificant deviation ($|z| < 10$) of water composition, H_2O_{1-z} , from the stoichiometric one ($z=0$). The hypo-stoichiometric state ($z > 0$) with the negative ORP is realized when Fermi level is shifted to the local donor level, ϵ_{HO} , by electro-reducing the aqueous coolant in the electrochemical cell with the strongly polarized anode and the quasi-equilibrium cathode, occupying ϵH_2O by electrons, and forming hydroxonium radicals, H_3O , as the strongest reducers. Opposite, the hyper-stoichiometric state ($z < 0$) with the positive ORP is realized in the electrochemical cell with the strongly polarized cathode and the quasi-equilibrium anode when Fermi level is shifted to the local acceptor level, radicals, ϵ_{OH} , as the strongest oxidizers. ϵ_{OH} , forming in water hydroxyl.

Keywords: Aqueous coolant; Non-stoichiometric water; Band gap; Fermi level; Oxidation-reduction potential

Introduction

A series of theoretical works on the electronic properties of liquid water have appeared in the present decade aided by the rapid increase in computational power [1]. In particular, a density of states (DOS) and a band gap as an energy difference which separates the occupied molecular orbital and the empty electronic states in the liquid water have merited the attention for fundamental studying. They are not understood quite in comparison with thermodynamics and structure of water, but they are very important for understanding water as participant and medium of chemical reactions. This medium is described as a dielectric with the broad band gap, $g=6.9$ eV [2] as a difference between electron energies at the top of valence band or a highest occupied molecular orbital and the bottom of conduction band as a lowest unoccupied molecular orbital. At the same time, there are two allowed local electron states in the band gap of liquid water such as an occupied-by-electron level, ϵ_{OH} , of hydroxide ion, OH^- , and the vacant one of hydroxonium cation, $\epsilon_{H_3O^+}$, located symmetrically nearby the band-gap middle with the energy difference between them of 1.75 eV [3]. This theoretical concept allows to eliminate the inconsistencies [4] in reconciling the electrochemical properties of these well known aqueous ions in the frame of electronic band structure [3]. For liquid water as a chemical compound of variable composition, it is useful to define a quantity called Fermi level, F [5,6] as an electrochemical potential which indicates the tendency of liquid water to donate or accept the proton. If ϵ_F is high, there is a strong tendency for liquid water to donate protons, i.e., it is reducing. Opposite, if Fermi level in aqueous medium is low, there is the strong tendency for it to accept protons when this matter is oxidizing [7]. Now, it is very important to understand what application of this approach can be used in practice. Just the solution of such the question is the subject of the present paper specifically electrochemical keeping the given quality of the aqueous coolant in power water reactors.

The band structure of liquid water

In according to [3] the liquid water contains the allowed energy levels, ϵ_{HO} and ϵ_{OH} , in the band gap for inherent constituents of liquid water as ions of hydroxonium, H_3O^+ and hydroxide, OH^- due to the reversible self-dissociation of liquid water by reaction [8].



Their radicals (H_3O , OH) as the hydrated hydrogen, $H \cdot H_2O$, and

half-oxygen, $(1/2) (O \cdot H_2O)$, are interpreted as the mentioned levels occupied by electrons and holes respectively and located symmetrically nearby the middle of the band gap (Figure 1) with $\epsilon_{HO} - \epsilon_{OH} = 1.75$ eV.

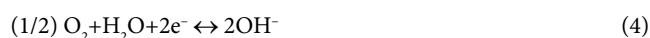
In general, the position of Fermi level ϵ_F in the band gap of dielectric is the threshold of 50% population of the all allowed electronic levels in its band gap. For the aqueous coolant, this level as the electrochemical potential [5–7] is a single-valued characteristic of water oxidation-reduction potential (ORP) [6]:

$$ORP = -(\epsilon_F - \epsilon_{SHE})/e \quad (2)$$

where $\epsilon_{SHE} = -6.21$ eV is the Standard Hydrogen Electrode [3] and e is the charge of electron.

ORP becomes negative when Fermi level is shifting to the donor level, ϵ_{H_2O} (Figure 1) which is occupied by electrons and forms hydroxonium radicals, H_3O , as the strongest reducers transforming water to hypo-stoichiometric one, H_2O_{1-z} , with $z > 0$. Opposite in the hyper-stoichiometric water ($z < 0$), Fermi level is shifted to the acceptor level, ϵ_{OH} , which forms hydroxyl radicals, ϵ_{OH} , as the strongest oxidizers and ORP is positive.

These states are easily realized in pure water by the following standard reactions [8]



The corresponding Fermi levels, $\epsilon_{F(2)}$ and $\epsilon_{F(3)}$, are shown in Figure 2 by red lines. It is known [9, 10] that the population [H_3O] and [OH] of the energy levels, ϵ_{HO} and ϵ_{OH} , by electrons and holes can be defined by the proportions of the species concentrations: [H_3O^+]/[H_3O] and [OH^-]/[OH], that are given by Maxwell–Boltzmann distribution of electrons and holes in the corresponding energy levels [3]

$$[H_3O^+]/[H_3O] = \exp[(\epsilon_{H_2O} - \epsilon_F)/k_B T], \quad (5)$$

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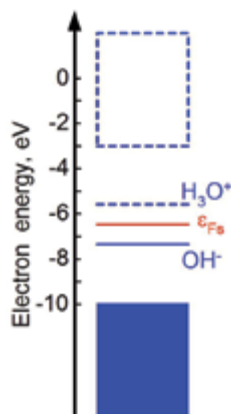


Figure 1: The band structure of stoichiometric liquid water with Fermi level (red line in the middle of band gap); the blue box is the valence band and the dotted one is the conduction bands; the full blue line denotes occupied-by-electrons energy level, ϵ_{OH^-} for hydroxide ions, OH^- and dotted blue line denotes the vacant one, for hydroxonium ions, H_3O^+

$$[OH]/[OH^-] = \exp[(\epsilon_{OH^-} - \epsilon_F) / k_B T] \quad (6)$$

FB where T is Kelvin temperature, and kB is Boltzmann constant equal to $8.62 \cdot 10^{-5}$ eV/K.

Then, using the molar concentrations, $[H_3O^+]$ and $[OH^-]$, of hydroxonium and hydroxide ions in the famous dissociation ratio [11].

$$[H_3O^+] \cdot [OH^-] = Kw \quad (7)$$

with the constant, $Kw = 10^{-14}$ M² at T=300 K, we can transform the index z of non-stoichiometric water, H_2O_{1-z}

$$z = 0.018 \{ [H_3O^+] - [OH^-] \} \quad (8) \text{ to the form}$$

$$z = 0.018 \{ \exp[(\epsilon_F - \epsilon_{HO}) / k_B T - 2.3pH] - \exp[(\epsilon_{OH} - \epsilon_F) / k_B T - 32.2 + 2.3pH] \} \quad (9)$$

$$\text{where } pH = -\lg[H_3O^+].$$

The composition confines of chemical water stability

As seen in Figure 2 Fermi level, $\epsilon_{F(3)}$ in hypo-stoichiometric water is controlled by the concentration of hydroxonium radicals, $[H_3O]$, as species of occupied-by-electrons level, ϵ_{HO} . At the same time, Fermi level, $\epsilon_{F(4)}$ of hyper-stoichiometric water is controlled by hydroxyl concentration $[OH]$. These non-stoichiometric states of liquid water are realized at $[H_3O^+] = [OH^-] = 10^{-7}$ M. In the case of T=300 K and

$$P_{H_2} = P_{O_2} = 1 \text{ atm}, [H_2] = 1.6 \cdot 10^{-3} \text{ M}, [O_2] = 2.7 \cdot 10^{-4} \text{ M} [12], [H_3O] \sim 2 \cdot 10^{-11} \text{ M} \text{ and } [OH] \sim 8 \cdot 10^{-13} \text{ M} [3]. \text{ Then, the Eq. (9) becomes}$$

$$z = 0.44 \cdot 10^{-16} \{ \exp[38.7\Delta_F - 2.3pH] - \exp[2.3pH - 38.7\Delta_F - 32.2] \}. \quad (10)$$

for $\epsilon_F = \epsilon_{Fs} + \Delta_p$, $\epsilon_{Fs} = -6.45$ eV, $\epsilon_{HO} = -5.58$ eV, $\epsilon_{OH} = -7.32$ eV [3], and $k_B T = 0.026$ eV. This equation allows to plot Fermi level in any aqueous solution as a function of its non-stoichiometry, z, as shown in Figure 3. One can see that the region of chemical water stability is shifted to the hypo-stoichiometric state, H_2O_{1-z} (z>0), of aqueous medium which is achieved easier in an acidic solution than in the basic one by least shifting Fermi level from the band-gap middle to the local donor level, ϵ_{HO} . Opposite, the hyper-stoichiometric one, H_2O_{1-z} (z<0), with a little variation of z is achieved easier in a basic solution than in the acidic one by shifting Fermi level from the band-gap middle to the local acceptor level, ϵ_{OH} . Such the consideration can be applied to the aqueous coolant of pressurized water reactors with operational parameters: T=600 K,

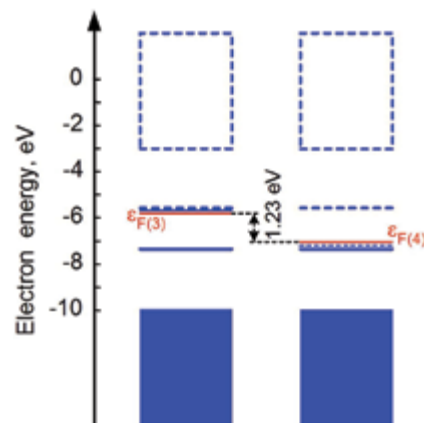


Figure 2: The non-stoichiometric states of liquid water with Fermi levels, $\epsilon_{F(3)}$ and $\epsilon_{F(4)}$, are realized in pure water at 300 K by the reactions (3) and (4) at pH=7; the full blue lines denote local occupied-by-electrons levels, ϵ_{HO} and ϵ_{OH^-} as hydroxonium radicals, H_3O , and hydroxide ions, OH^- ; dotted ones denote hydroxonium ions, H_3O^+ , and hydroxyls, OH .

$$P_{H_2} = P_{O_2} = 160 \text{ atm. Then, we will have } [H_2] = 7.7 \cdot 10^{-2} \text{ M},$$

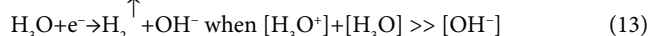
or $[O_2] = 1.8 \cdot 10^{-3}$ M [12], $[H_3O] = 1.4 \cdot 10^{-10}$ M or $[OH] \sim 2 \cdot 10^{-12}$ M, and Eq. (10) is transformed to

$$z = 0.98 \cdot 10^{-9} \{ \exp[19.2\Delta_F - 2.3pH] - \exp[2.3pH - 19.2\Delta_F - 26.45] \}. \quad (11)$$

for $k_{BT} = 0.052$ eV. One can see that here the region of chemical water stability by order of magnitude is greater than in Figure 3. At the same time, Fermi level as a function of water non-stoichiometry, z, at 600 K is more conservative than at 300 K and more sensitive to aqueous-solution type due to its line bundle. At the same time as seen in Figures 3 and 4, the quick response of Fermi level to changing the water non-stoichiometry, z, in the stoichiometric point (z=0) takes place at 600 K as well as at 300 K. Therefore, a little additive of any oxidant or antioxidant in pure water changes its ORP (Fermi level) appreciably. It is interesting to note that such the effect can be gotten without chemical additives by electro-oxidizing (or electro-reducing) the pure liquid water in a special electrochemical cell with one polarized electrode and the other in equilibrium with the aqueous medium.

Electro-oxidation of the pure liquid water

As seen in Figure 3, the region of liquid-water chemical stability is defined by the very narrow range $-10^{-14} \leq z < 4 \cdot 10^{-13}$ of non-stoichiometric composition, H_2O_{1-z} , and changing Fermi level in the band gap up to 2 eV. The forced variation of ϵ_F can be carried out by the electrochemical cell with the voltage of ~2 V between the strongly polarized cathode and the anode in quasi-equilibrium [13]. This can change physical and chemical properties of pure liquid water as well as its ORP up to the ones of a strong acid by keeping liquid water in the hypo-stoichiometric state (z>0) when the external potential applied to the strongly polarized cathode intensively generates hydroxide ions, OH^- , in the narrow layer of unstable liquid water of near the cathode (Figure 5) by reactions:



At the same time, Fermi level is shifting to the energy level, ϵ_{OH} , and the hydroxide ions forcedly migrate in the bulk of water due to the action of electric field. They are discharged to hydroxyls by quasi-equilibrium anodic reaction [13]

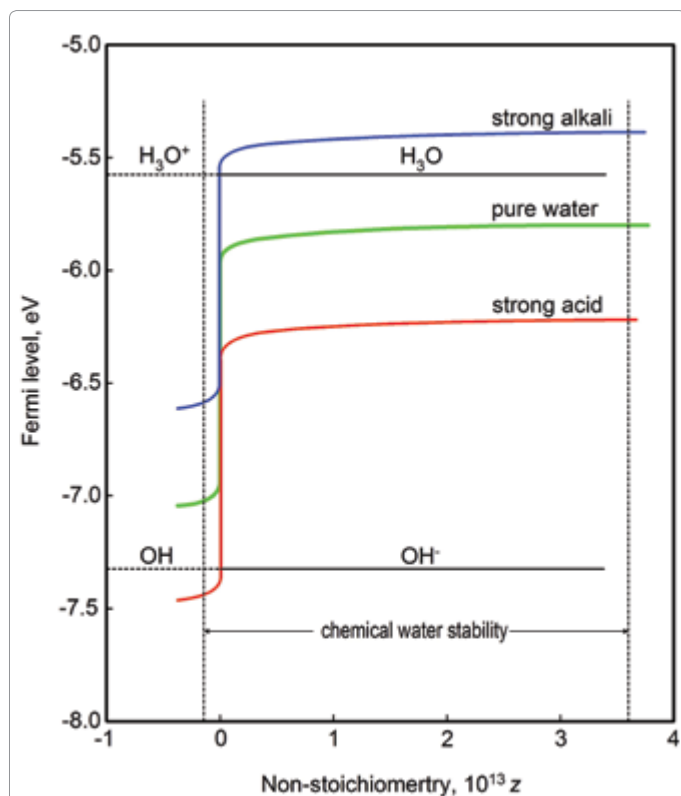


Figure 3: Fermi level as a function of non-stoichiometry, z , in pure liquid water, H_2O_{1-z} (green line), in the aqueous solution of strong alkali (blue line), and the solution of strong acid (red line) at $T=300$ K and $P=1$ atm; dotted vertical lines denote the composition confines of chemical water stability and the horizontal lines denote the local energy levels, $\epsilon_{H_3O^+}$ and ϵ_{OH} , for hydroxonium, H_3O^+ / H_3O , and hydroxyl, H/OH^- respectively.



but hydroxonium radicals, H_3O , diffused out of the cathode layer (Figure 5) of electrochemical cell put electrons to hydroxyl radicals by reaction



All this forms the positive bulk charge in liquid water near the cathode (Figure 5) at the condition

$$[H_3O^+] > [OH] \gg [OH^-] > [H_3O] \quad (16)$$

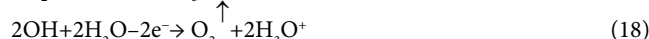
which indicate on the strong acidic reaction of the chemically stable hypo-stoichiometric water with the high mole fraction ($[OH] \gg 10^{-7}$ M) of hydroxyls as the strongest oxidizers (Table 1).

The advantage of this approach is the high efficiency of oxidation reaction, the simplicity of the procedure, low cost, and there is no need for special sorbents because water itself becomes the agent for oxidizing pollutants [13,14]. Thus, the electrochemical oxidation with the advantage of environmental compatibility is the promising procedure for removing pollutants from waste water by hydroxyl radicals produced on the quasi-equilibrium anode out of hydroxide ions electro-generated by the strongly polarized cathode. It is very important to generate them intensively since the life-time of hydroxyl radicals is very short (only few nanoseconds) [15] due to quick forming the solvated acceptors of electrons by bulk reaction.

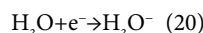
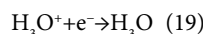


Electro-reducing the pure liquid water

Changing the polarity of the electrochemical cell, we will get the strongly polarized anode and the cathode in quasi-equilibrium and by applied potential, convert the hyper-stoichiometric unstable water ($z < 0$) in the anode layer (Figure 6) in the hypo-stoichiometric state ($z > 0$) by reactions [16].



One can see that Fermi level is shifting higher the energy level, ϵ_H O, and the hydroxonium ions forcedly migrate in the bulk of water due to the action of electric field. This gives the basic properties for processed liquid water which is kept in the stable hypo-stoichiometric state by negative charge formed in the bulk and cathode layer by quasi-equilibrium cathode reactions [16].



because a little part of hydroxyl radicals, OH, diffuses in the bulk out of the anode layer of electrochemical cell. All this forms the negative bulk charge in liquid water near the anode (Figure 6) at the condition

$$[H_3O^-] + [H_3O] > [OH^-] \gg [H_3O^+] \gg [OH] \quad (22)$$

Oxidizer	ORP, V
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Oxygen (molecular)	1.23

Table 1: Oxidation potential of chemical oxidants [14].

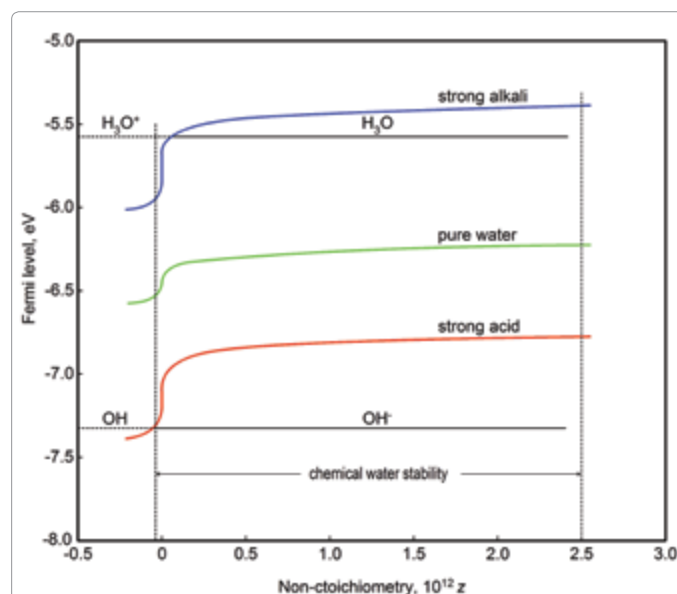


Figure 4: Fermi level as a function of non-stoichiometry, z , in pure liquid water, H_2O_{1-z} (green line), in the aqueous solution of strong alkali (blue line), and the solution of strong acid (red line) at $T=600$ K and $P=160$ atm; dotted vertical lines denote the composition confines of chemical water stability and the horizontal lines denote the local energy levels, $\epsilon_{H_3O^+}$ and ϵ_{OH} , for hydroxonium, H_3O^+ / H_3O , and hydroxyl, OH/OH^- respectively.

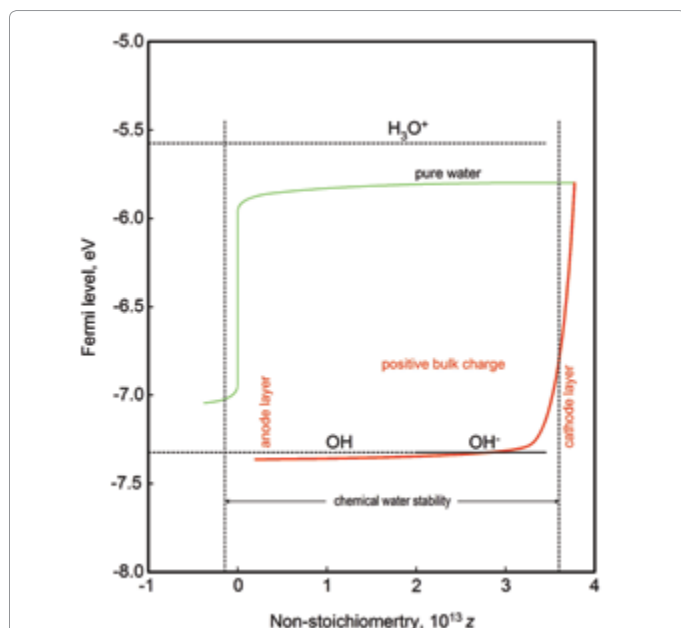


Figure 5: The change of Fermi levels of the initial non-stoichiometric pure liquid water, H_2O_{1-z} (green line in Figure 3) by the electrochemical cell with the voltage of 2V between the strongly polarized cathode and the quasi-equilibrium anode (red line) at $T=300$ K and $P=1$ atm; dotted vertical lines denote the composition confines of chemical water stability and the horizontal lines denote the local energy levels, $\epsilon_{H_3O^+}$ and ϵ_{OH^-} for hydroxonium ions, H_3O^+ , and hydroxyl/hydroxide species, OH/OH^- respectively.

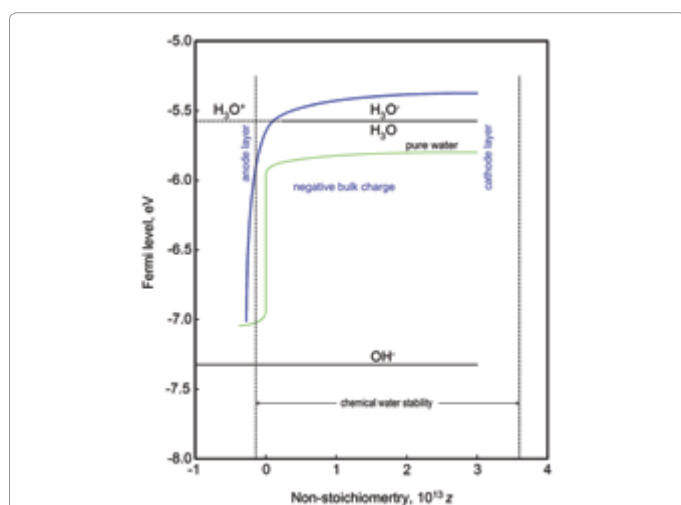


Figure 6: The change of Fermi levels of the initial non-stoichiometric pure liquid water, H_2O_{1-z} (green line in Figure 3) by the electrochemical cell with the voltage of 2 V between the strongly polarized anode and the quasi-equilibrium cathode (blue line) at $T=300$ K and $P=1$ atm; dotted vertical lines denote the composition confines of chemical water stability and the horizontal lines denote the local energy levels, $\epsilon_{H_3O^+}$ and ϵ_{OH^-} for hydroxonium species, H_3O^+ , H_3O/H_3O^- , and hydroxide anions OH^- respectively.

which indicate on the strong basic reaction of the chemically stable hypo-stoichiometric water with the high mole fraction ($[H_3O^-] + [H_3O] \gg 10^{-7}$ M) of the hydride anions as proton acceptors and the hydroxonium radicals as electron donors in the bulk of water [16].

Thus, electrochemical production of these very active antioxidants can be more effective than the gaseous hydrogen can do them in the aqueous coolant ($[H_3O] \sim 10^{-10}$ M) for holding the negative ORP of hydrogen water chemistry in PWR.

Discussion of results

The plot of Fermi levels in the non-stoichiometric aqueous medium is differed essentially from the one in the electrochemical cell with one strongly polarized electrode and the other in quasi-equilibrium as seen in the Figures 5 and 6. The mechanisms for forming oxidizers, $[OH]$, or reducers, $[H_3O]$, are also differed: in aqueous emulsion of gases, they are formed by kinetically-limited reactions of dissociation:



but in the electrochemical cell, they are generated without limitation by reactions (14) and (19) that essentially increases their molar portion in liquid water. It can change the current aqueous chemistry of PWR which is the oxidative one in essence due to continuous feed water additives naturally containing oxygen. This impurity is not desirable for the PWR first-loop coolant due to the continuous growth of oxide films on the surface of fuel cladding. Therefore, it is important to organize an effective technological process for removing oxygen from the feed water by converting ORP of the aqueous coolant in the negative region (2) and obtain the corrosion-passive one that can inhibit the growth of oxide films on the surface of fuel cladding and local break-up of them. Thus, pH and ORP mechanism are independent in processing liquid water. The first can be changed in stoichiometric water, H_2O , by adding equivalent amount of anions and cations. The second can be changed without changing pH in ventilating the pure liquid water by bubbles of oxygen (hydrogen) or by processing the initial aqueous medium in the electrochemical cell with one strongly polarized electrode and the other in quasi-equilibrium. Since non-stoichiometry of H_2O_{1-z} varies at very narrow interval of $|z| \leq 10^{-12}$ (Figure 4), ORP is highly sensitive to external conditions and can change without visible varying a composition of the aqueous medium. Therefore online monitoring ORP (Fermi level) by precise sensor is very important [6].

Conclusions

It is shown that the region of chemical water stability is shifted to the hypo-stoichiometric state, H_2O_{1-z} ($z > 0$), of aqueous medium which is achieved easier in an acidic solution than in the basic one by least shifting Fermi level from the band-gap middle to the local donor level, $\epsilon_{H_3O^+}$. Opposite, the hyper-stoichiometric one, H_2O_{1-z} ($z < 0$), with a little variation of z is achieved easier in a basic solution than in the acidic one by shifting Fermi level from the band-gap middle to the local acceptor level, ϵ_{OH^-} . It turned out that the interval of chemical stability of the PWR coolant is greater by order of magnitude than the one for water at the room temperature as well as more conservative and more sensitive to aqueous-solution type. At the same time, the quick response of Fermi level to changing the water non-stoichiometry, z , takes place in the stoichiometric state ($z=0$). Therefore, a little additive of oxidant or antioxidant in pure water changes ORP (Fermi level) appreciably. Such the effect may be gotten also by electro-oxidizing (electro-reducing) liquid water in the electrochemical cell with one polarized electrode and the other in equilibrium with the aqueous medium. Thus, the electrochemical oxidation with the advantage of environmental compatibility can become the effective method for removing pollutants from wastewater by hydroxyl radicals produced on the quasi-equilibrium anode out of hydroxide ions electro-generated by the strongly polarized cathode. In turn, the electrochemical production of very active reducers, H_3O and H_3O^- , can be more effective for maintaining the negative ORP in PWR coolant than the gaseous hydrogen in feed water can do this.

Acknowledgements

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