Supplementary Information

Thermodynamics of the glycerol oxidation reaction: effect of temperature, pH, applied potential, and concentration

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Supplementary note 1 – Derivation of thermodynamic model

The equations implemented to calculate the effect of pH and reactant-product concentration on the oxidation potential of the different reaction pathways of the glycerol oxidation network, were derived from the definition of the Gibbs free energy of reaction (Eq. S2). The transition from Eq. S3 to S4 uses the definition of pH = -$\log_{10}$ H^+.

$$rR + mH_2O \rightleftharpoons pP + hH^+ + ne^- \quad \text{Eq. S1}$$

$$\Delta_{rxn}G\,(pH) = \Delta_{rxn}G^\circ\,(pH) + RT\ln\frac{P^p * H^{+h}}{R^r} \quad \text{Eq. S2}$$

$$\Delta_{rxn}G\,(pH) = \Delta_{rxn}G^\circ(pH) + RT\left(\ln\frac{P^p}{R^r} + \ln H^{+h}\right) \quad \text{Eq. S3}$$

$$\Delta_{rxn}G\,(pH) = \Delta_{rxn}G^\circ(pH) + RT\left(\ln\frac{P^p}{R^r} - h * \ln 10 * pH\right) \quad \text{Eq. S4}$$

$$E\,(pH) = \frac{\Delta_{rxn}G(pH)}{nF} \quad \text{Eq. S5}$$

$$E\,(pH) = E^\circ\,(pH) + \frac{RT}{nF}\left(\ln\frac{P^p}{R^r} - h * \ln 10 * pH\right) \quad \text{Eq. S6}$$

To evaluate the effect of applied potential on the distribution of products, Eq. S6 can be rearranged in the following way:

$$\ln\frac{P^p}{R^r} = \ln Q = \frac{[E(pH) - E^\circ\,(pH)] * nF}{RT} + h * \ln 10 * pH \quad \text{Eq. S7}$$

The calculation of $^{\Delta_{rxn}G^\circ(pH)}$ and h will be explained in the **Supplementary note 2**. For the data in Figure 2, the calculations were done at standard conditions: 1 bar, 298.15 K, unitary activity coefficient and pH 0. Consequently, only the standard Gibbs free energy of reaction $(\Delta_{rxn}G^\circ)$ and standard enthalpy of reaction $(\Delta_{rxn}H^\circ)$ were used. Here *p* stands for product and *r* stands for reactant. The Gibbs free energy and enthalpy of formation of the different molecules can be found in Tables S2 and S3.

$$\Delta_{rxn}G^\circ = \sum_i \nu_i * \Delta_f G^\circ_{p,i} - \sum_j \nu_j * \Delta_f G^\circ_{r,j} \quad \text{Eq. S8}$$

$$\Delta_{rxn}H^\circ = \sum_i \nu_i * \Delta_f H^\circ_{p,i} - \sum_j \nu_j * \Delta_f H^\circ_{r,j} \quad \text{Eq. S9}$$

$$E^\circ = \frac{\Delta_{rxn}G^\circ}{nF} \quad \text{Eq. S10}$$

$$E^\circ_{th} = \frac{\Delta_{rxn}H^\circ}{nF} \quad \text{Eq. S11}$$

Supplementary note 2 – Speciation plots, $^{\Delta_{rxn}G^\circ(pH)}$, h

Acid or alkaline molecules tend to deprotonate or protonate as a function of pH and their respective pKas. In speciation plots, the relative fraction of the protonated and deprotonated species is plotted as a function of pH. For monoprotic acids (Eq. S12) the fraction of protonated species is given by the pKa and Eq. S13, while the deprotonated fraction is given by Eq. S14. For diprotic acids (Eq. S15) the fraction of the protonated species is given by Eq. S16, the first deprotonation is given by Eq. S17, and the fully deprotonated species is given by Eq. S18.

$$HA \rightleftharpoons A^- + H^+ \quad \text{Eq. S12}$$

$$f_{HA} = \frac{1}{1 + 10^{pH - pKa}} \quad \text{Eq. S13}$$

$$f_{A^-} = 1 - f_{HA} \quad \text{Eq. S14}$$

$$H_2A \rightleftharpoons HA^- + H^+ \rightleftharpoons A^{2-} + H^+ \quad \text{Eq. S15}$$

$$f_{H_2A} = \frac{1}{1 + 10^{pH - pKa_1} + 10^{2pH - pKa_1 - pKa_2}} \quad \text{Eq. S16}$$

$$f_{HA^-} = f_{H_2A} * 10^{pH - pKa_1} \quad \text{Eq. S17}$$

$$f_{A^{2-}} = f_{HA} * 10^{2pH - pKa_1 - pKa_2} \quad \text{Eq. S18}$$

The different fractions of protonated and deprotonated species are used to calculate the weighted average of the standard Gibbs free energy of formation, considering the effect of pH ($^{\Delta_f G^\circ(pH)}$,Eq. S19) and the weighted average of the stoichiometric coefficient *h*, for the release of H^+ (Eq. S20). The latter is the sum of two contributions: a constant number of H^+ released by the electrochemical oxidation

(h_{const}), and the pH dependent quantity of H^+ released due to the acid behaviour of the molecules involved in the reaction ($h_{acid,}$ Eq. S21).

$$\Delta_f G°(pH) = f_{H_2A} * \Delta_f G°_{H_2A} + f_{HA^-} * \Delta_f G°_{HA^-} + f_{A^{2-}} * \Delta_f G°_{A^{2-}} \quad \text{Eq. S19}$$

$$h(pH) = h_{const} + h_{acid_{products}}(pH) - h_{acid_{reactants}}(pH) \quad \text{Eq. S20}$$

$$h_{acid}(pH) = f_{H_2A} * 0\ H^+ + f_{HA^-} * 1H^+ + f_{A^{2-}} * 2H^+ \quad \text{Eq. S21}$$

The Gibbs free energy of formation of the conjugated base (anions) was calculated using Hess's Law, which states that the total Gibbs free energy change (state function) of a chemical reaction is the same, regardless of the number of steps or path taken. Therefore, if a reaction can be broken into multiple steps, the overall Gibbs free energy change of the reaction is just the sum of the Gibbs free energy changes of those steps. Since we are working using the SHE as the reference point, the $\Delta_f G°_{H^+}$ is zero.

$$HA \rightleftharpoons A^- + H^+ \quad \text{Eq. S22}$$

$$\Delta_{rxn} G° = RT \ln K_a \quad \text{Eq. S23}$$

$$\Delta_{rxn} G° = \left(\Delta_f G°_{A^-} + \Delta_f G°_{H^+}\right) - \Delta_f G°_{HA} \quad \text{Eq. S24}$$

$$\Delta_f G°_{A^-} = \Delta_{rxn} G° + \Delta_f G°_{HA} - \Delta_f G°_{H^+} \quad \text{Eq. S25}$$

The pKa of all the molecules of the GOR network are displayed in **Table S1**. They were taken from different sources[2–7]. This pKa was used to calculate the Gibbs free energy of formation (**Table S2**) and the speciation plots of the deprotonated species (**Fig. S1-S13**)

Supplementary note 3 – Specific energy consumption calculation

The specific energy consumption (SEC) is used to quantify the amount of energy in kWh needed to produce 1 kg of hydrogen. When calculated using the $\Delta_{rxn} G°$, it provides the thermodynamic limit for the minimum amount of energy needed to produce hydrogen for the specified reaction. For the case of water splitting it is common to use the cell voltage and quantity of produced hydrogen to calculate the efficiency of the process by comparing with the SEC from the $\Delta_{rxn} G°$.

$$SEC\left(\frac{kWh}{kg\ H_2}\right) = \frac{Total\ electrical\ energy\ consumed}{Mass\ of\ hydrogen\ produced} \quad \text{Eq. S26}$$

$$SEC = \frac{\Delta_{rxn} G°\ or\ \Delta_{rxn} H°\ \left(\frac{J}{mol}\right)}{moles\ of\ H_2\ produced * H_2\ molar\ mass\left(\frac{kg}{mol}\right)} * \frac{1\ kWh}{3.6\ 10^6\ J} \quad \text{Eq. S27}$$

Table S1. pKa value of the different molecules involved in the GOR network.

	pKa 1	pka 2
GLY	14.15	
DHA	13.5	
GLAD	12.84	
LAC	3.86	
GLAC	3.52	
HPAC	2.39	
TAC	2.42	4.54
MESAC	1.56	3.6
GCAD	14.27	
AcOH	4.756	
GAC	3.83	
GLYX	3.18	
OXAC	1.25	3.81
FAC	3.75	
H_3CO_3	6.35	10.33

Table S2. Gibbs free energy of formation of glycerol, its oxidation products, and their respective conjugated bases, at 298.15 K and 1 bar. Where there is more than one pKa the first deprotonation is showed in the first row, followed by the second deprotonation. For the case of carbonic acid (H_3CO_3) since the more stable phase in acidic media is CO_2, this is the value reported for the *HA*. The deprotonated species, present in alkaline media, are bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). The Gibbs free energy of formation of the protonated species were taken from our previous work[1].

Species	units	$\Delta_f G°_{HA}$	$\Delta_f G°_{anion}$
GLY	J/mol	-485093	-404325
DHA	J/mol	-451202	-374144
GLAD	J/mol	-445897	-372606
LAC	J/mol	-526419	-504386
GLAC	J/mol	-702030	-681938
HPAC	J/mol	-692513	-678871
TAC	J/mol	-911982	-898169
			-872254
MESAC	J/mol	-888635	-879731
			-859182
GCAD	J/mol	-264076	-182623
AcOH	J/mol	-387695	-360548
GAC	J/mol	-529248	-502100
GLYX	J/mol	-488616	-470465
OXAC	J/mol	-688919	-681784
			-660037
FAC	J/mol	-358146	-336741
H_2CO_3	J/mol	-384888	-586770
			-528080

Table S3. Enthalpy of formation of glycerol, its oxidation products, water, hydrogen and oxygen at 298.15 K and 1 bar. Enthalpy data was calculated in the method specified in our previous work[1].

Species	units	$\Delta_f H°$
WATER	J/mol	-285818
CO_2	J/mol	-397800
GLY	J/mol	-667400
DHA	J/mol	-568051
FAC	J/mol	-398592
GAC	J/mol	-663257
GCAD	J/mol	-371546
GLAC	J/mol	-839054
OXAC	J/mol	-800365
TAC	J/mol	-1042248
HPAC	J/mol	-761475
MESAC	J/mol	-998725
GLYX	J/mol	-539364
GLAD	J/mol	-568051
H_2	J/mol	0
O_2	J/mol	0

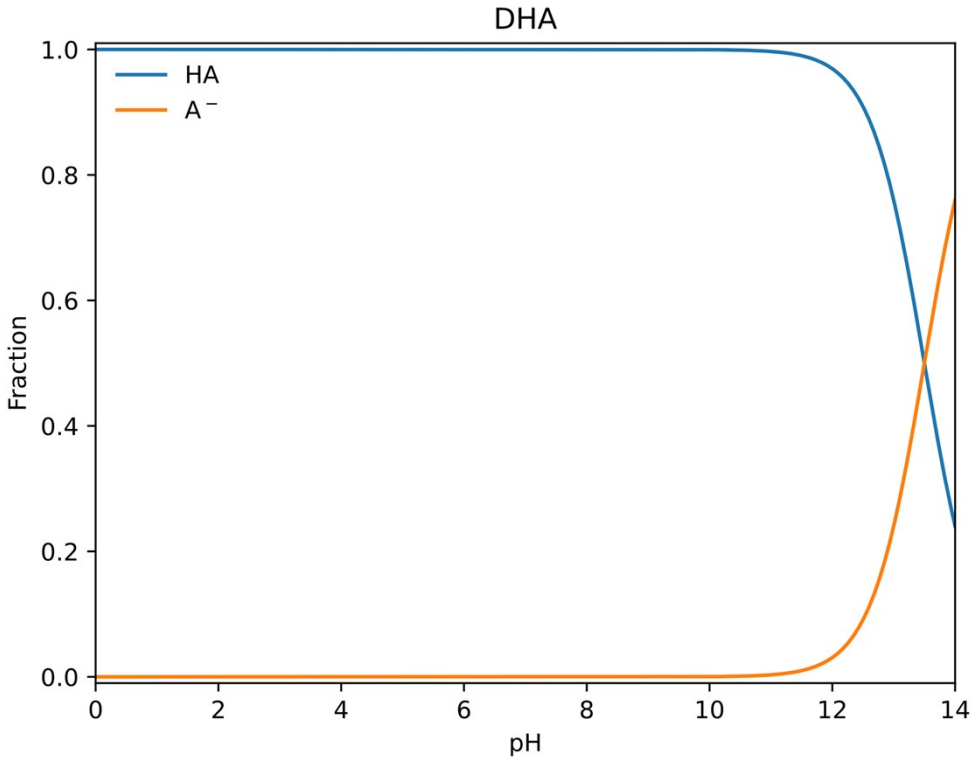

Figure S1. Speciation plot of dihydroxyacetone (DHA*)*

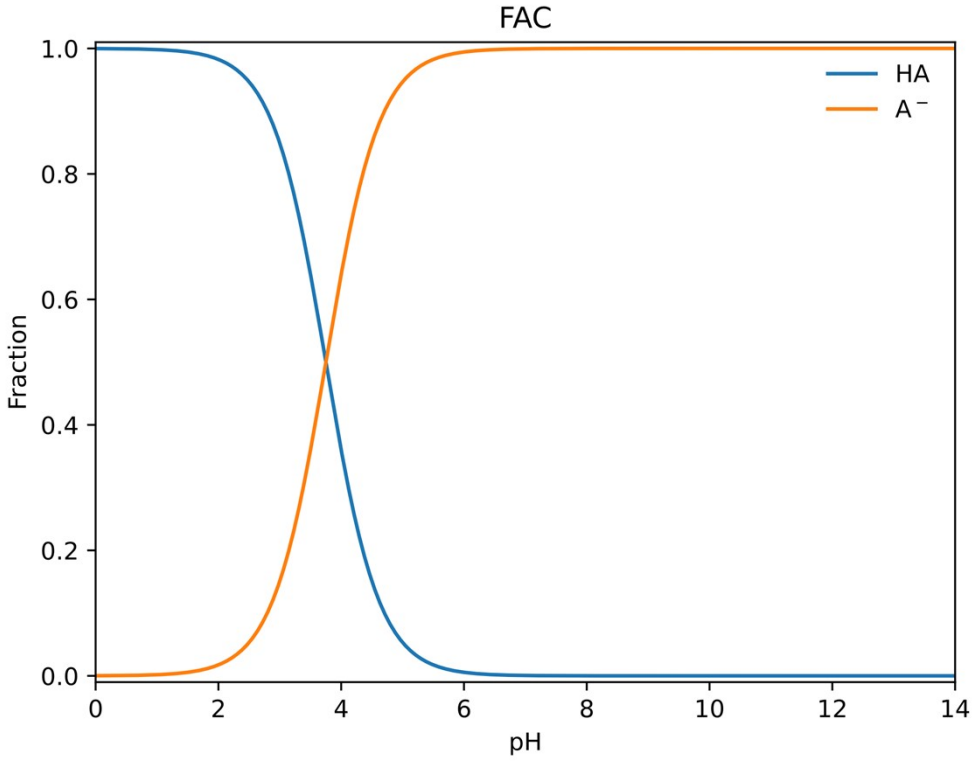

Figure S2. Speciation plot of formic acid (FAC)

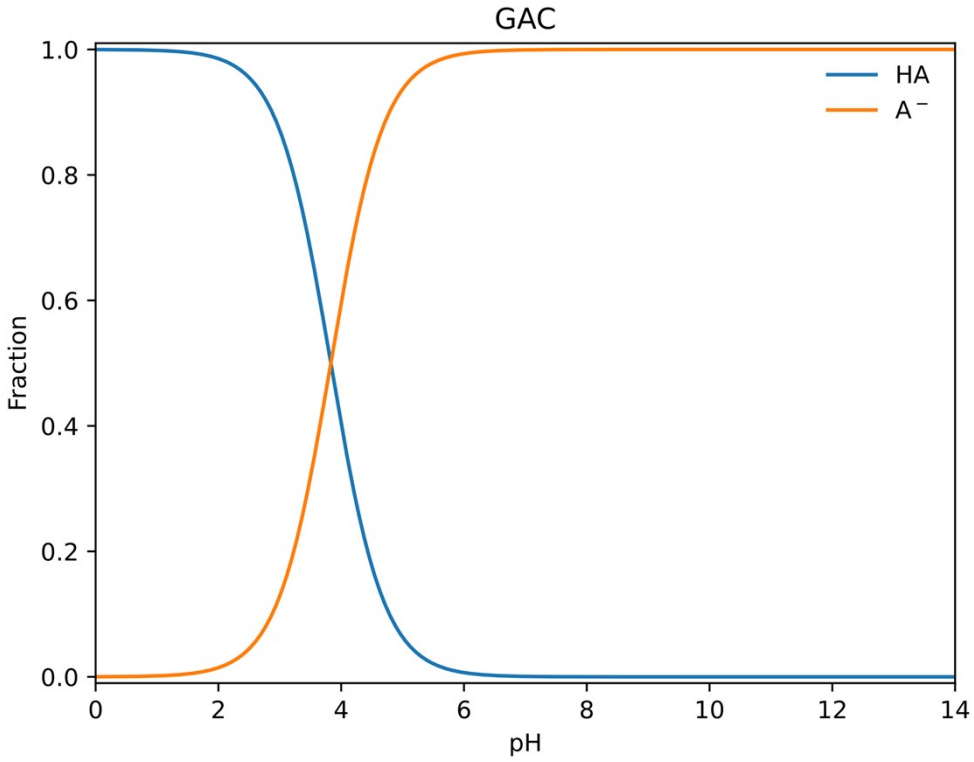

Figure S3. Speciation plot of glyceric acid (GAC)

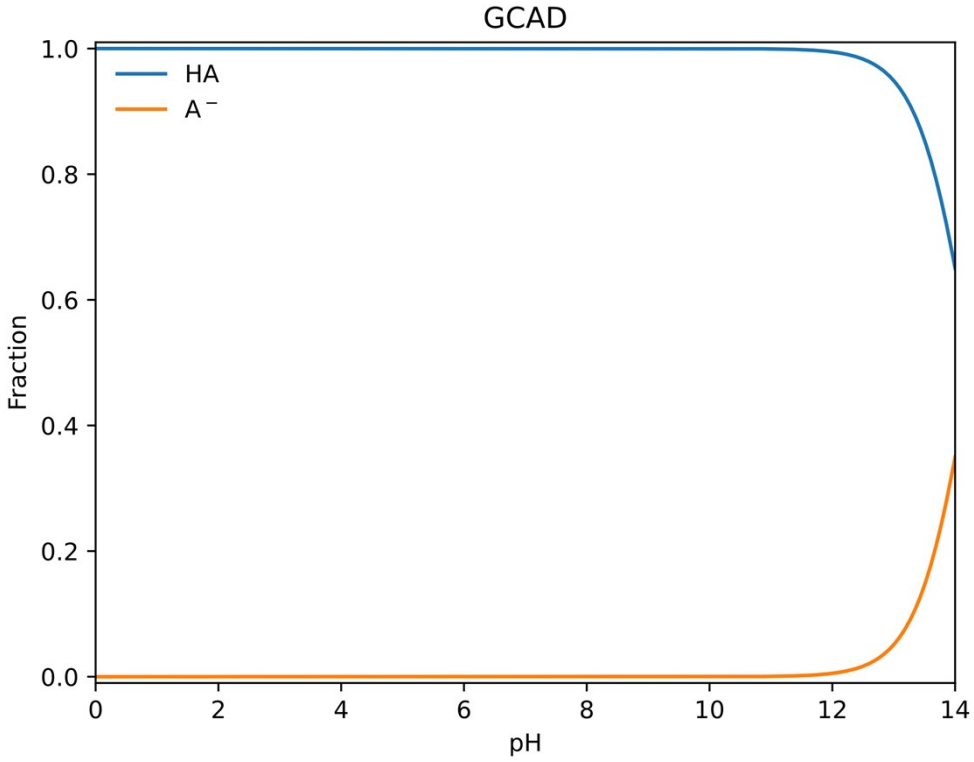

Figure 4. Speciation plot of glycolaldehyde (GCAD)

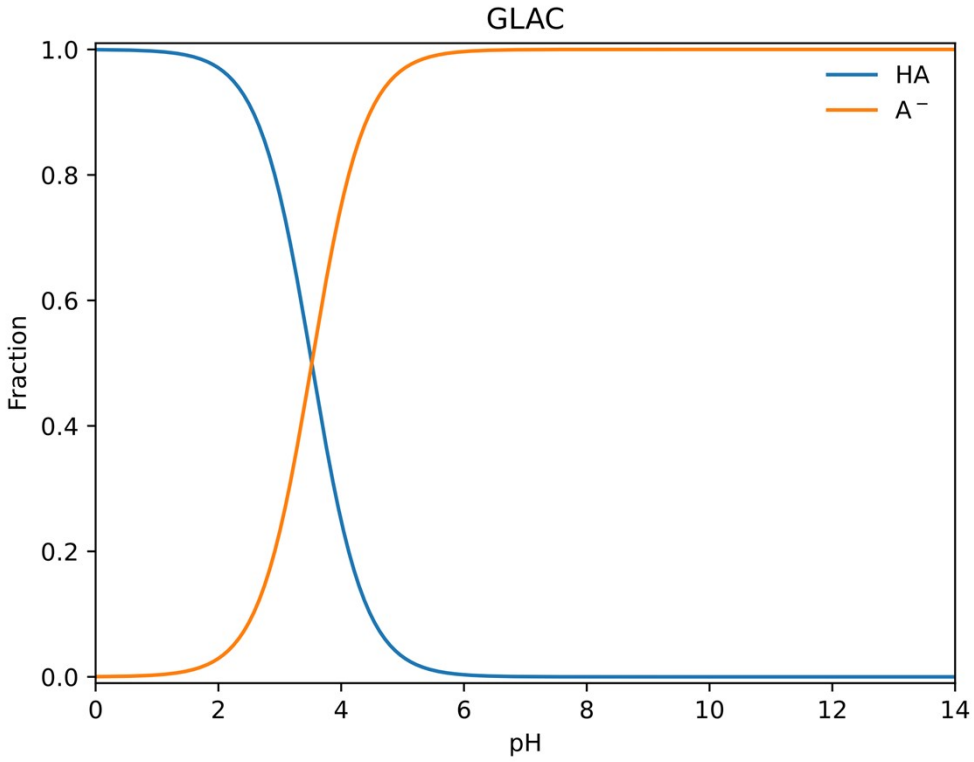

Figure S5. Speciation plot of glyceric acid (GLAC)

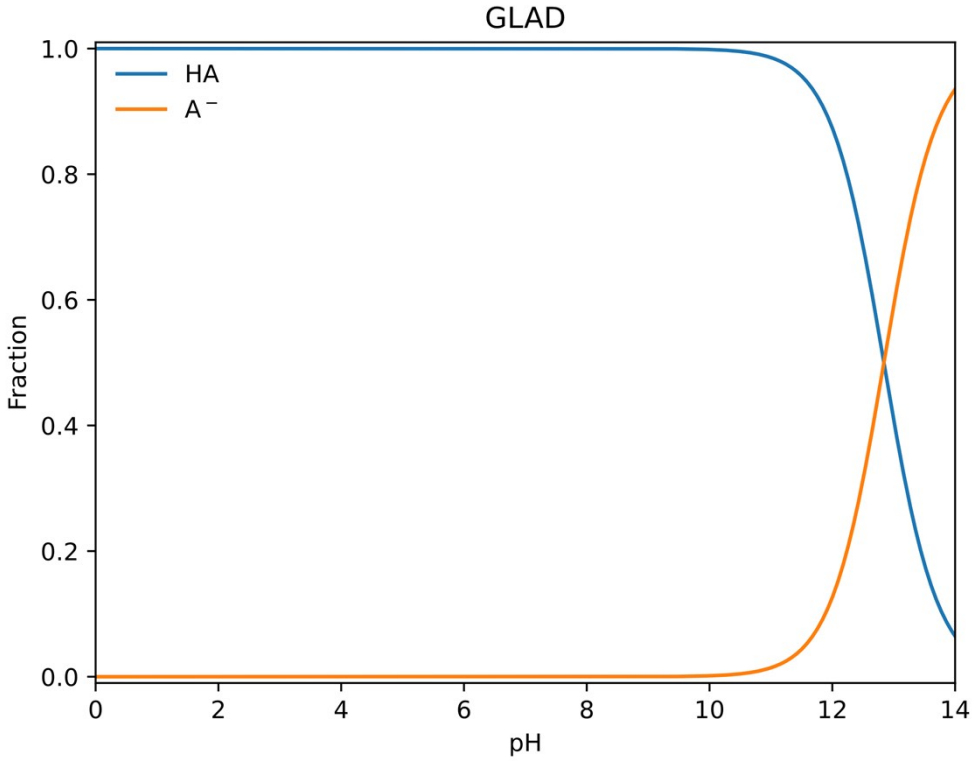

Figure S6. Speciation plot of glyceraldehyde (GLAD)

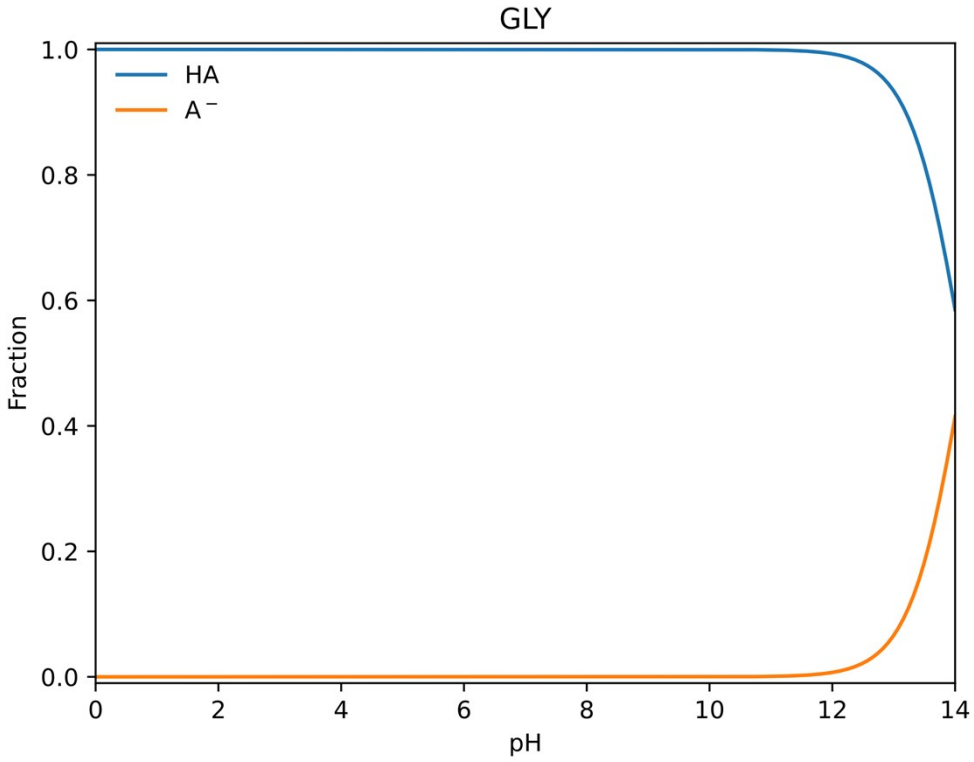

Figure S7. Speciation plot of glycerol (GLY)

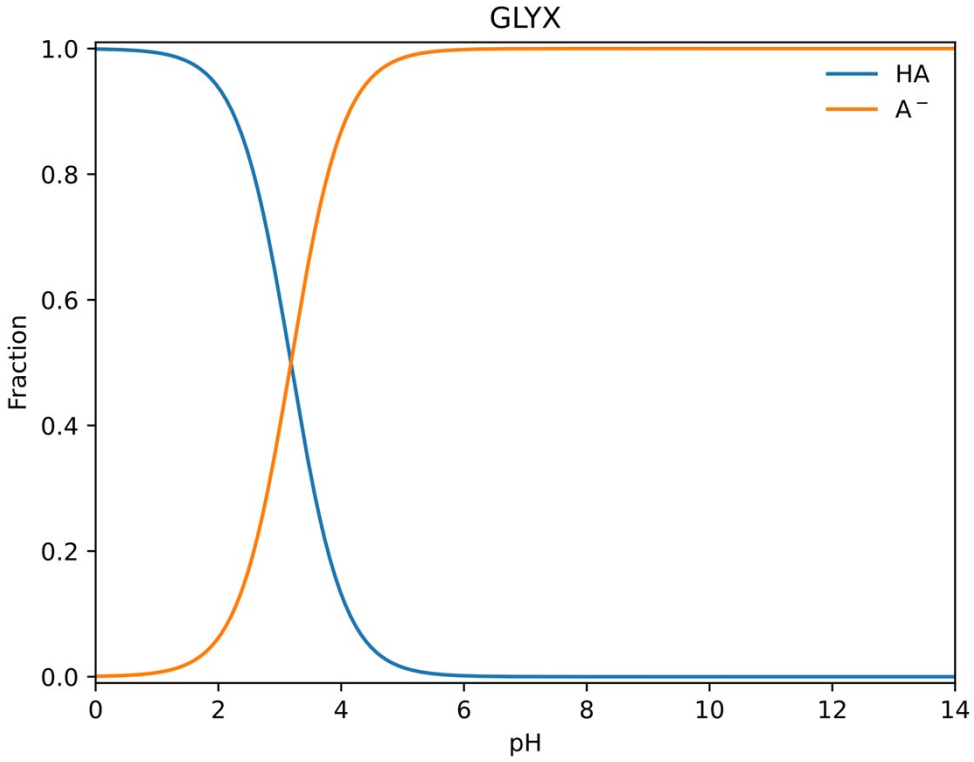

Figure S8. Speciation plot of glyoxylic acid (GLYX)

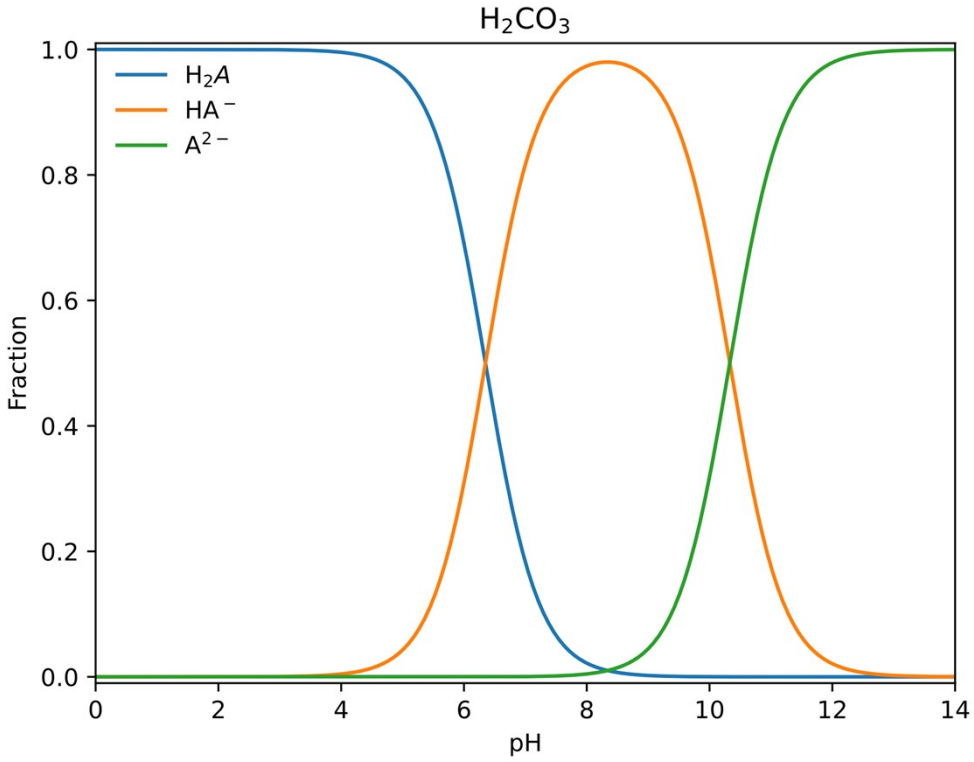

Figure S9. Speciation plot of carbonic acid

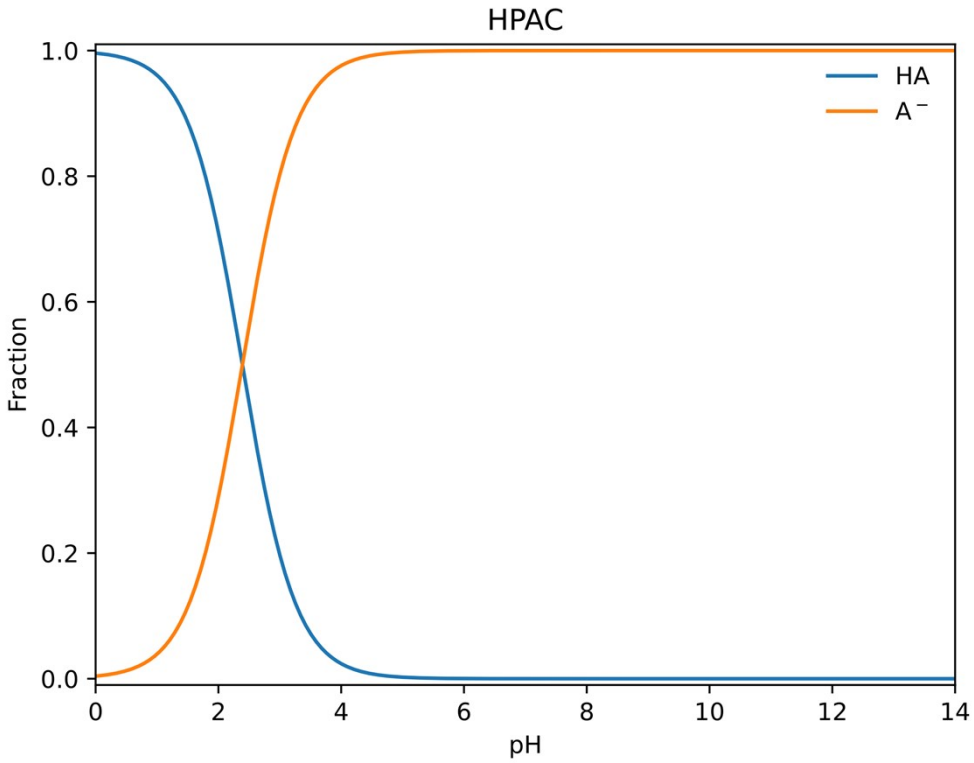

Figure S10. Speciation plot of hydroxypyruvic acid (HPAC)

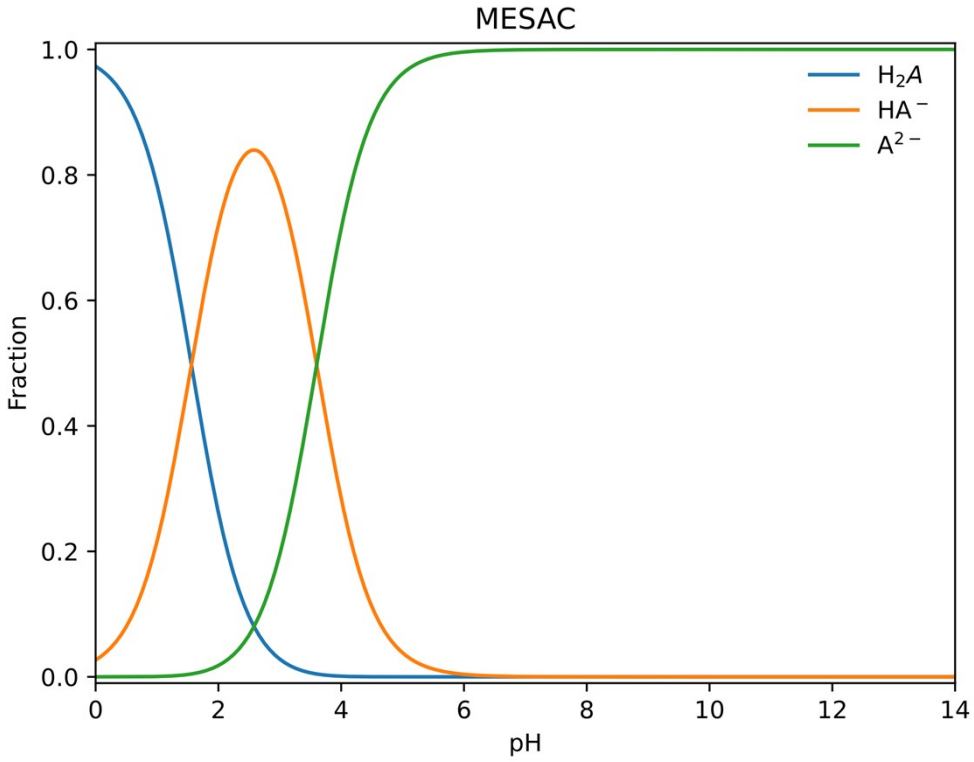

Figure S11. Speciation plot of mesoxalic acid (MESAC)

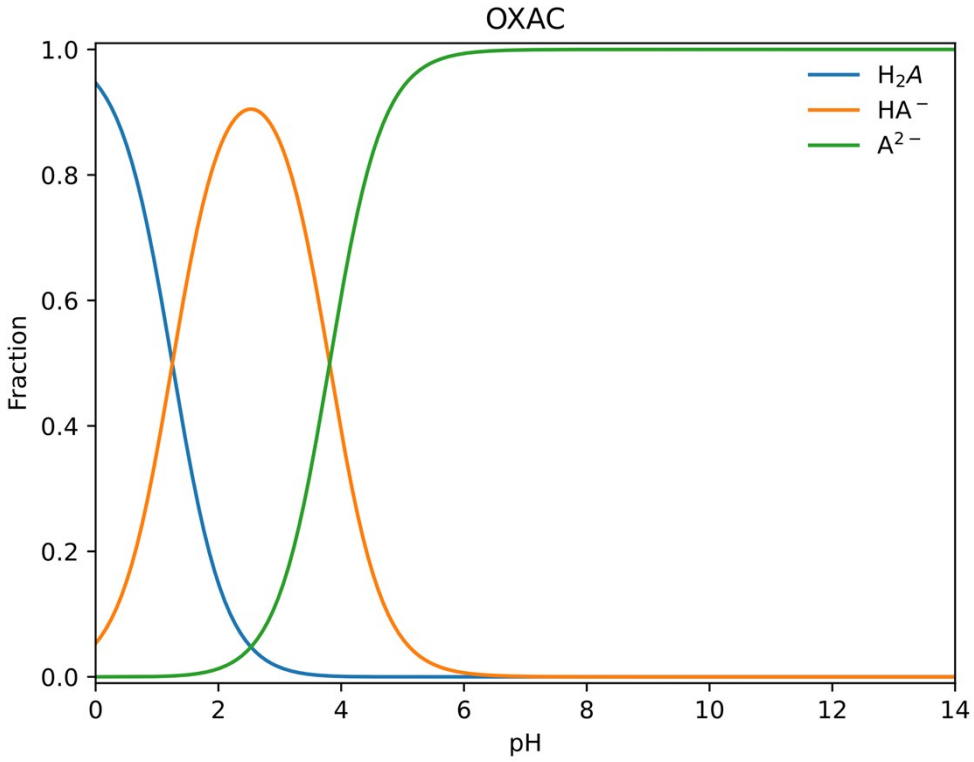

Figure S12. Speciation plot oxalic acid (OXAC)

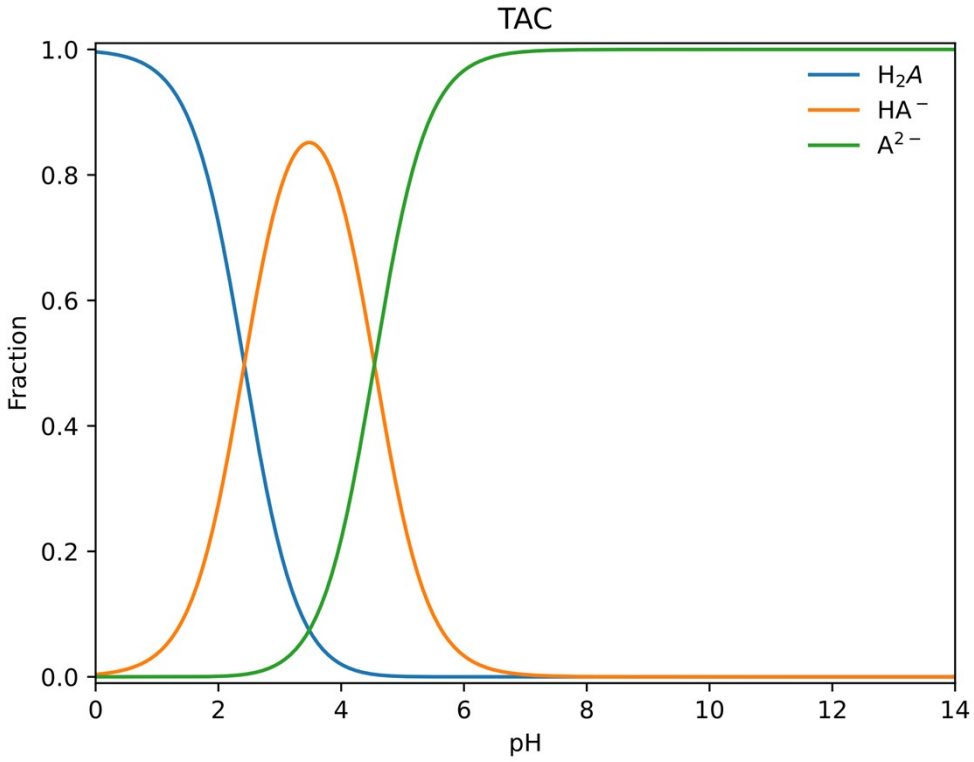

Figure S13. Speciation plot of tartronic acid (TAC)

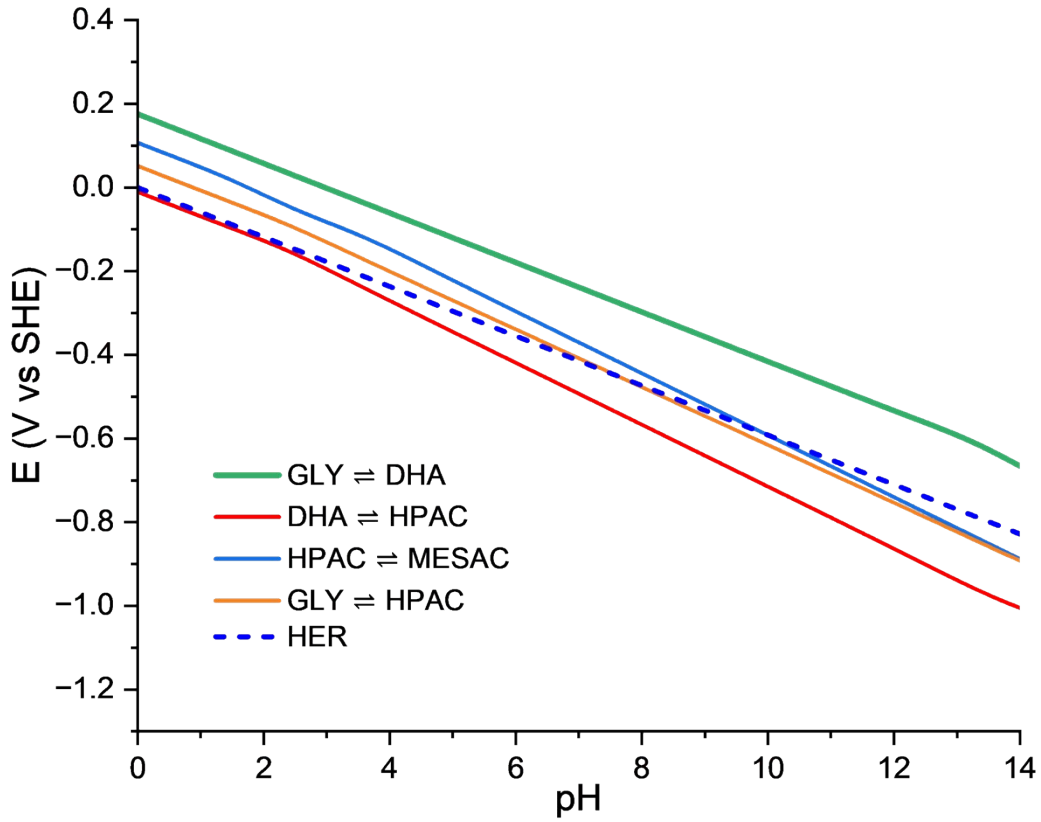

Figure S14. Potential-pH relationships for the C_3 to C_3 oxidation reaction, DHA pathway.

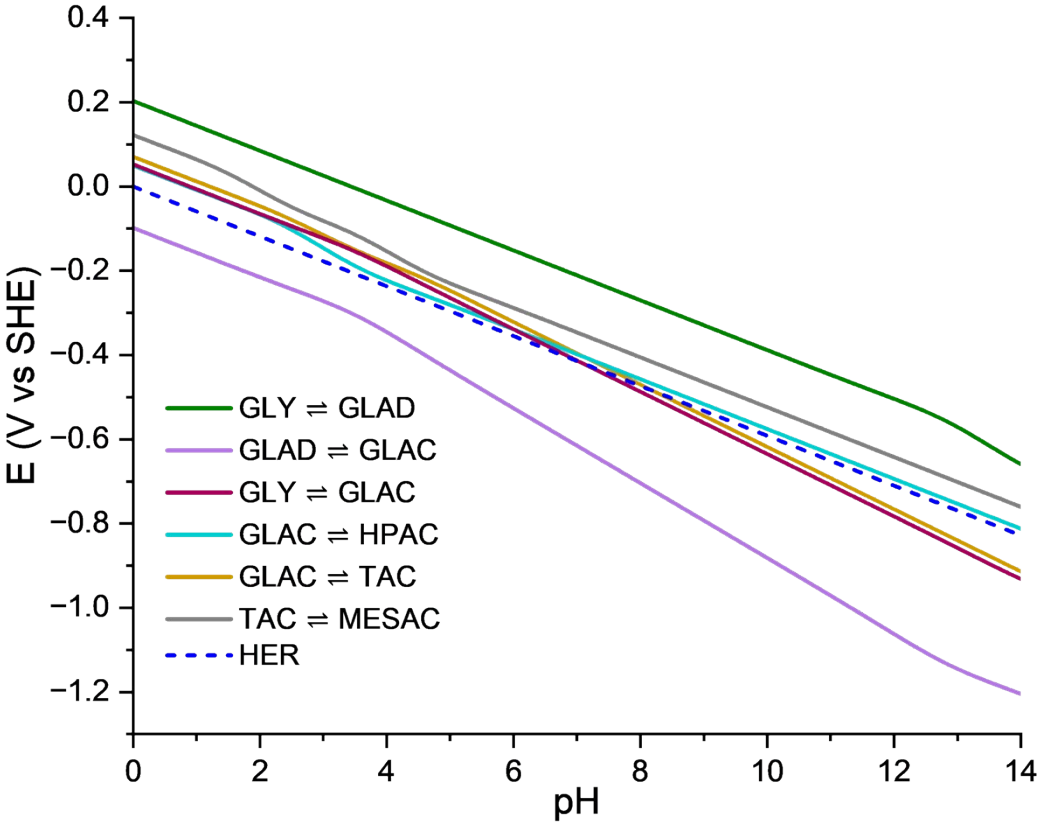

Figure S15. Potential-pH relationships for the C_3 to C_3 oxidation reaction, GLAD pathway.

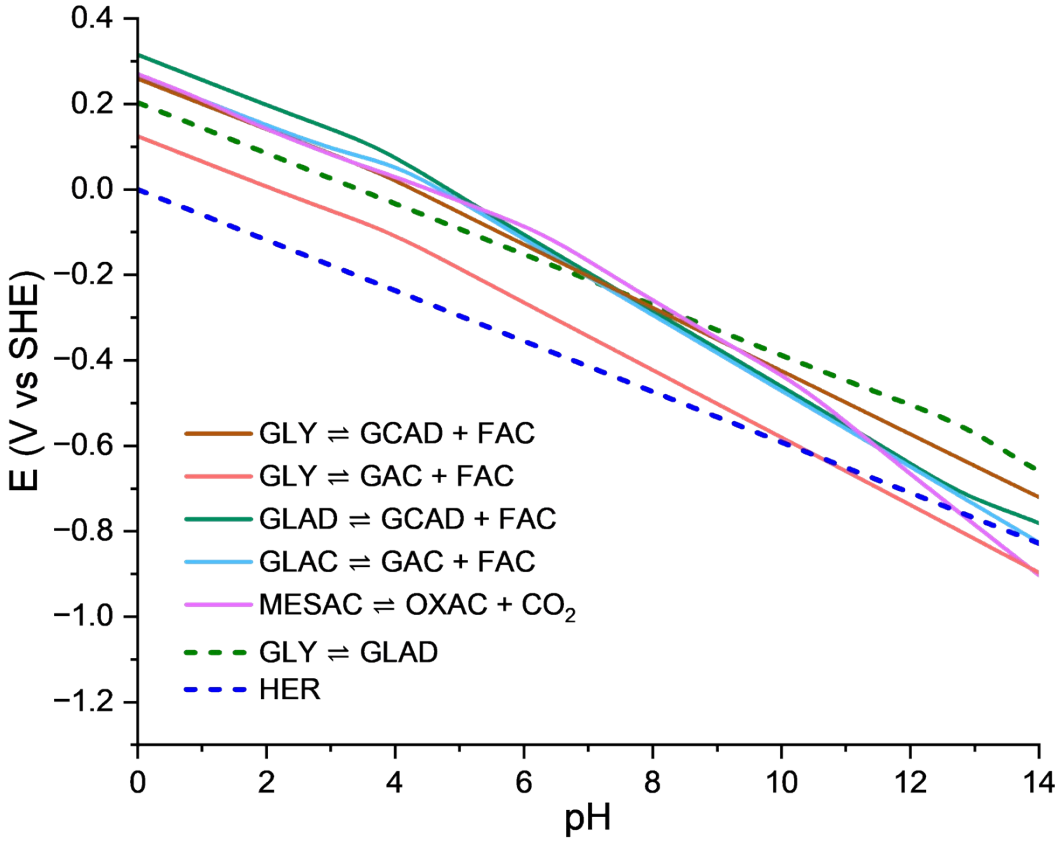

Figure S16. Potential-pH relationships for the oxidation pathway of C_3 to C_2 and C_1.

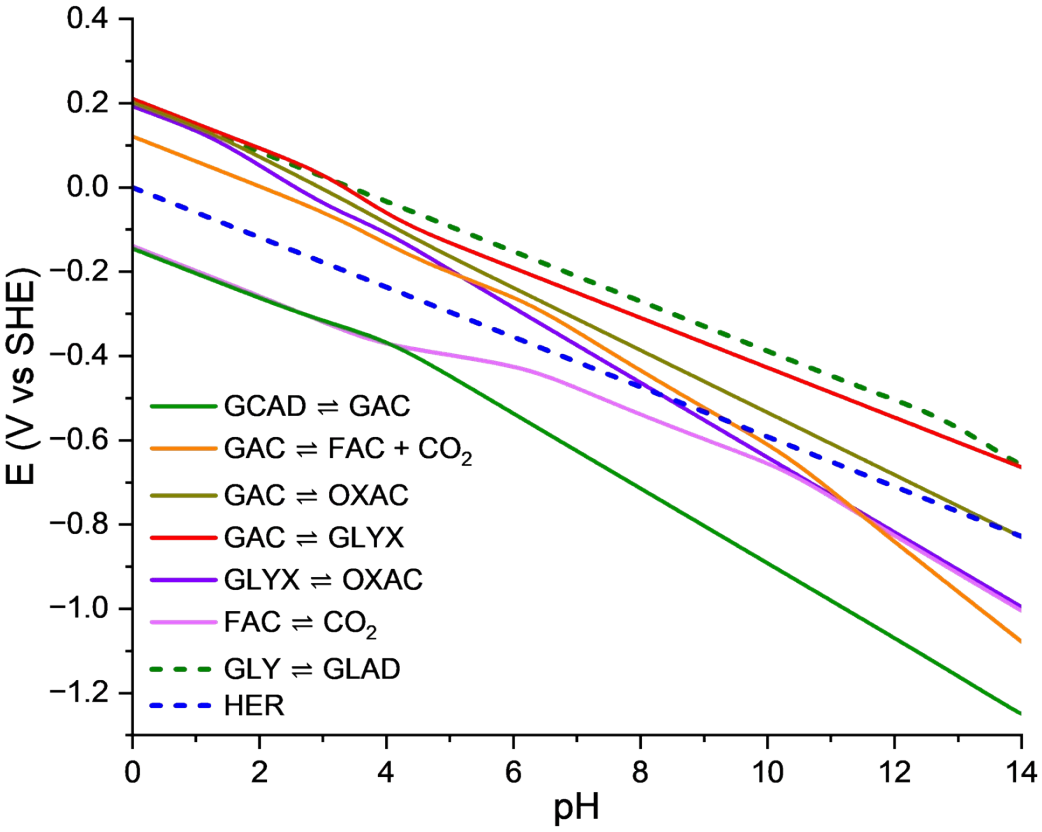

Figure S17. Potential-pH relationships for the oxidation pathway of C_2 to C_2 and C_1.

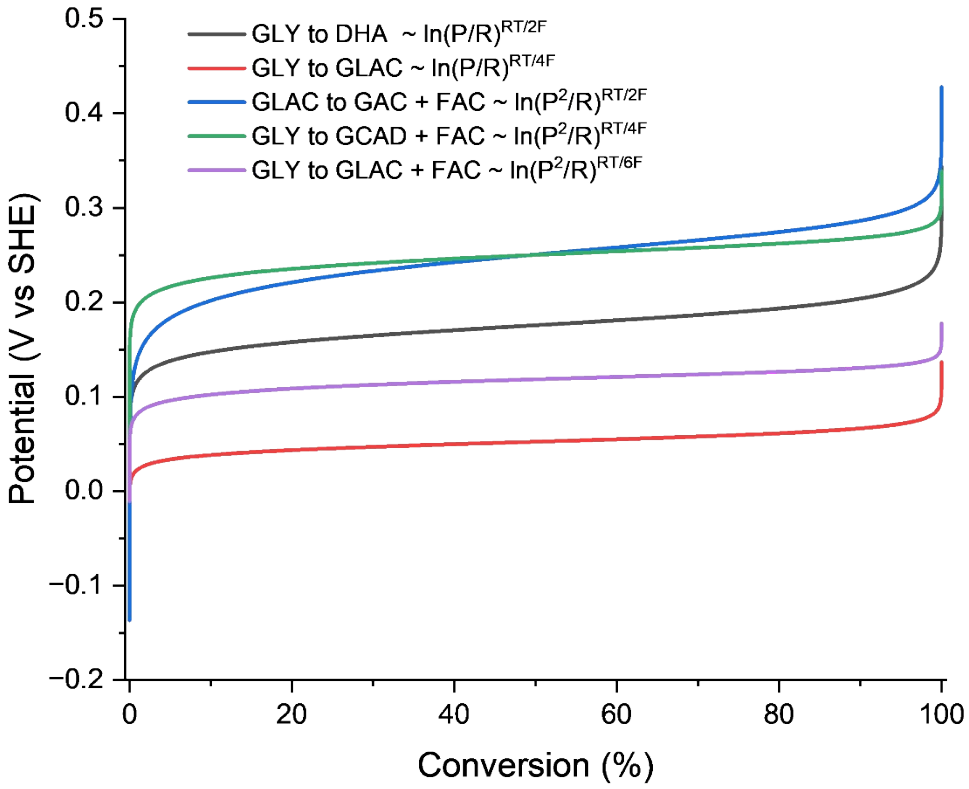

Figure S18. Effect of reaction conversion on the oxidation potential at pH 0 and room temperature (298.15 K).

References:

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