Supporting Information

Potential Dependence of Gluconic Acid to Glucose Electroreduction on Silver

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E / V vs RHE	c_0(Gluconic acid) / mmol L^{-1}	c_0(Glucose) / mmol L^{-1}	t / h	c(Gluconic acid) / mmol L^{-1}	c(Glucose) / mmol L^{-1}	$c(Glucose)_{prod.}$ / mmol L^{-1}	CR(Gluconic acid) / %	Q / C	FE / %
−0.66	127.89	0.121	1	127.76	0.127	0.006	0.005	34	0.17
			2	127.84	0.128	0.007	0.006	70	0.10
			4	127.87	0.128	0.007	0.006	135	0.05
			6	127.55	0.128	0.007	0.006	193	0.04
			8	127.56	0.130	0.009	0.007	247	0.04
	129.63	0.125	8	132.84	0.136	0.008	0.006		
			AV 8			0.008	0.007		
−0.86	127.91	0.121	1	127.83	0.132	0.012	0.009	51	0.21
			2	127.65	0.132	0.012	0.009	104	0.11
			4	128.32	0.136	0.015	0.012	198	0.07
			6	127.79	0.136	0.015	0.012	284	0.05
			8	127.69	0.139	0.018	0.014	359	0.05
	128.83	0.124	8	131.35	0.139	0.012	0.009		
			AV 8			0.015	0.012		
−1.06	128.05	0.118	1	128.30	0.133	0.015	0.011	59	0.23
			2	128.23	0.140	0.022	0.017	110	0.19
			4	128.05	0.161	0.043	0.033	195	0.21
			6	127.87	0.172	0.054	0.042	269	0.19
			8	128.47	0.188	0.069	0.054	335	0.19
	127.37	0.123	8	131.60	0.175	0.049	0.037		
			AV 8			0.059	0.046		
−1.16	127.46	0.125	1	127.46	0.148	0.022	0.017	62	0.33
			2	128.22	0.160	0.035	0.027	127	0.26
			4	130.64	0.197	0.070	0.053	240	0.27
			6	130.64	0.221	0.094	0.073	334	0.26
			8	129.91	0.247	0.120	0.092	417	0.27
	128.70	0.122	8	128.53	0.237	0.115	0.089		
			AV 8			0.117	0.091		
−1.26	128.98	0.122	1	127.68	0.134	0.013	0.011	63	0.20
			2	127.75	0.140	0.019	0.015	126	0.15
			4	127.72	0.182	0.061	0.048	235	0.25
			6	127.82	0.211	0.090	0.070	325	0.26
			8	128.04	0.259	0.138	0.107	402	0.33
	125.11	0.122	8	130.02	0.287	0.159	0.122		
			AV 8			0.148	0.115		
−1.36	128.17	0.123	1	128.03	0.163	0.040	0.031	58	0.65
			2	129.09	0.189	0.064	0.050	117	0.51
			4	128.35	0.244	0.120	0.093	217	0.52
			6	129.26	0.283	0.158	0.122	299	0.49
			8	128.89	0.310	0.185	0.144	370	0.47
	127.96	0.124	8	130.19	0.348	0.221	0.170		
			AV			0.203	0.157		

			8						
−1.46	127.44	0.121	1	127.92	0.209	0.088	0.069	59	1.39
			2	128.48	0.249	0.128	0.099	119	1.01
			4	129.18	0.315	0.193	0.149	224	0.80
			6	129.03	0.351	0.229	0.177	317	0.67
			8	129.33	0.377	0.254	0.196	397	0.60
	129.36	0.124	8	128.83	0.374	0.250	0.194		
			AV 8			0.252	0.195		
−1.56	126.34	0.122	1	125.73	0.290	0.168	0.133	58	2.72
			2	125.72	0.326	0.204	0.162	117	1.65
			4	125.31	0.377	0.255	0.203	225	1.08
			6	125.18	0.407	0.286	0.228	323	0.84
			8	126.01	0.420	0.298	0.236	411	0.69
	126.19	0.120	8	126.95	0.415	0.293	0.231		
			AV 8			0.296	0.233		
−1.66	128.29	0.129	1	128.66	0.265	0.136	0.105	55	2.31
			2	129.83	0.292	0.162	0.124	113	1.34
			4	127.96	0.325	0.197	0.153	228	0.82
			6	128.88	0.336	0.206	0.159	326	0.59
			8	128.86	0.337	0.208	0.161	413	0.47
	128.22	0.124	8	133.61	0.312	0.183	0.137		
			AV 8			0.195	0.149		

II. Supplemental Equation

The calculations of the Faraday efficiencies (FEs) for each timeline experiment were done according to Equation S1:

$$FE = \frac{z \cdot F \cdot n}{I \cdot t} = \frac{z \cdot F \cdot n}{Q} = \frac{z \cdot F \cdot c(Glucose)_{prod.} \cdot \frac{c_0(Glucose) + c_0(Gluconic\ acid)}{c(Glucose) + c(Gluconic\ acid)} \cdot V_0}{Q} \cdot 100\%$$

Eq. S1

where z, F and n represent the number of electrons for the conversion of gluconic acid to glucose ($2e^-$), the Faraday constant (96485 $C \cdot mol^{-1}$) and the mole of glucose generated, respectively. I is the current during the electrolysis (A) and t is the reaction time (s). Q is the charge passed during the electrolysis (C). $c(Glucose)_{prod.}$ is the produced glucose concentration ($mol \cdot L^{-1}$). $c_0(Glucose)$ is the initial concentration of glucose and $c_0(Gluconic\ acid)$ is the initial concentration of gluconic acid ($mmol \cdot L^{-1}$). $c(Glucose)$ and $c(Gluconic\ acid)$ are the measured glucose and gluconic acid concentrations after the reaction, respectively. V_0 is the initial volume of the catholyte solution (49 mL) and V the volume after the reaction.

III. Supplemental Figures

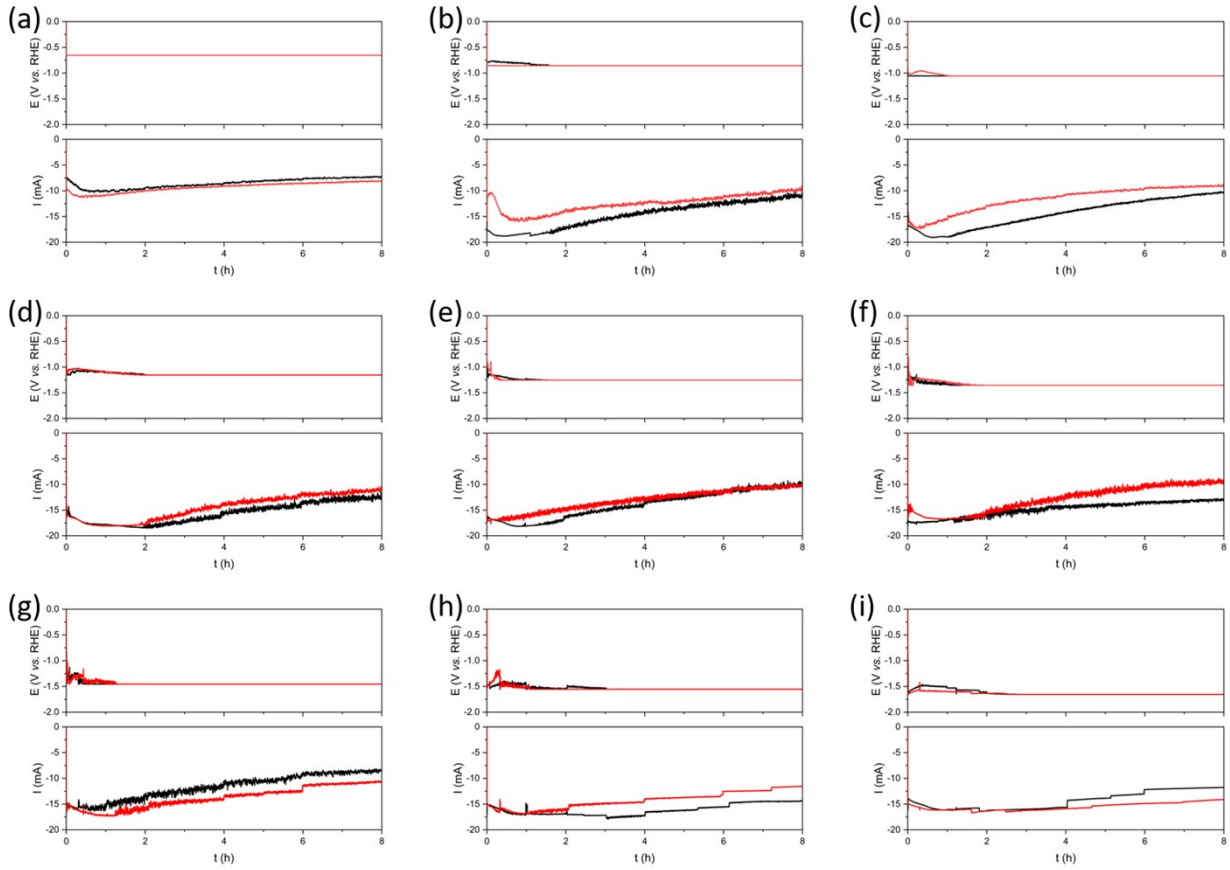

Figure S1. Chronoamperometric curves of 2.5 wt% gluconic acid and 1.5 wt% MgSO4 solution in the H-cell. As setup an Ag working electrode (geometric surface area 3.5 cm^2), a Pt counter electrode and an Ag/ AgCl (saturated KCl) reference electrode was used. Over the reaction time of 8 hours the reaction potentials were (a) −0.66 V *vs.* RHE (b) −0.86 V *vs.* RHE (c) −1.06 V *vs.* RHE (d) −1.16 V *vs.* RHE (e) −1.26 V *vs.* RHE (f) −1.36 V *vs.* RHE (g) −1.46 V *vs.* RHE (h) −1.56 V *vs.* RHE and (i) −1.66 V *vs.* RE. Duplicates of the reactions at each potential were performed. The potential *versus* the reaction time is shown in the upper part of each diagram and the corresponding current *versus* the reaction time in the lower part.

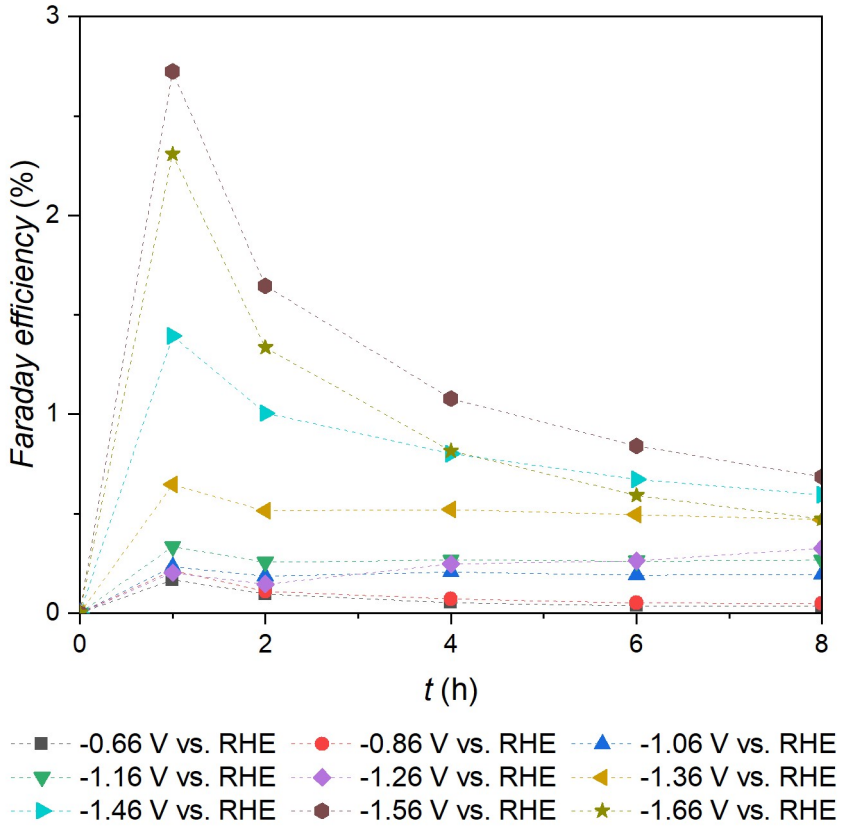

Figure S2. The curves show the Faraday efficiency over the reaction time up to 8 h. A 2.5 wt% gluconic acid and 1.5 wt% MgSO4 solution in an H-cell was used. As setup, an Ag working electrode (geometric surface area 3.5 cm^2), a Pt counter electrode and an Ag/ AgCl (saturated KCl) reference electrode were used. Over the reaction time of 8 h, the reaction potentials were −0.66 V *vs.* RHE (black), −0.86 V *vs*. RHE (red), −1.06 V *vs*. RHE (blue), −1.16 V *vs*. RHE (green), −1.26 V *vs*. RHE (purple), −1.36 V *vs*. RHE (beige), −1.46 V *vs*. RHE (turquoise), −1.56 V *vs*. RHE (brown) and −1.66 V *vs.* RE (olive).

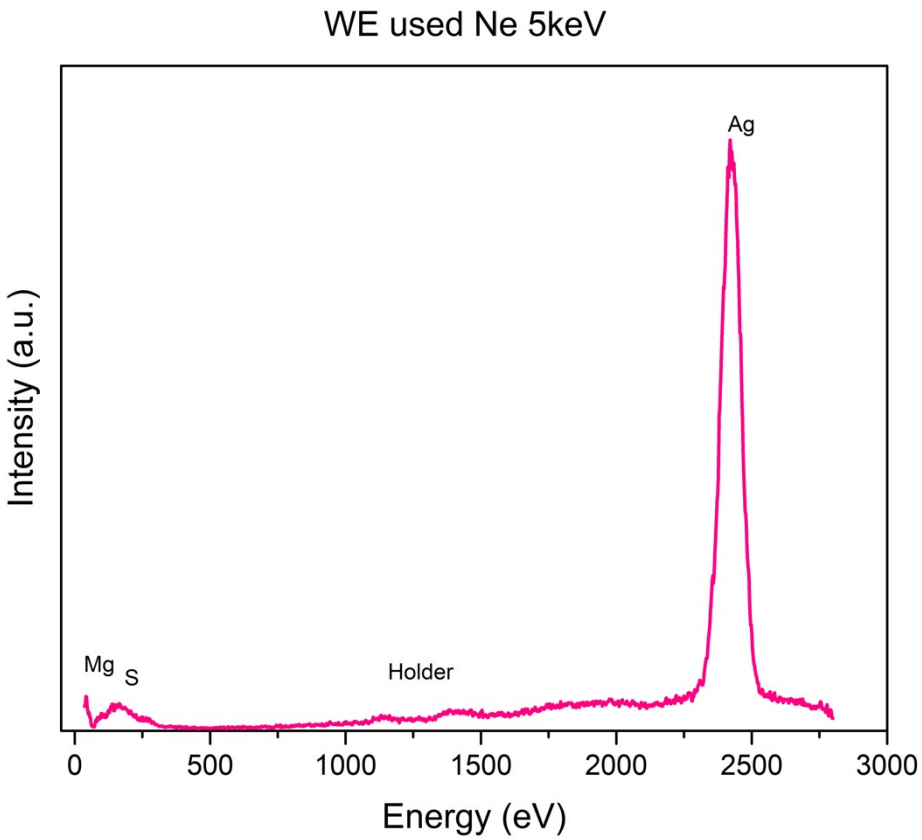

Figure S3. LEIS spectrum of the silver working electrode after the reaction in the H-cell. The reaction was performed in a 2.5 wt% gluconic acid solution with 1.5 wt% $MgSO_4$. The reaction time was 8 h and a 3-electrode setup with an Ag/AgCl (KCl saturated) reference electrode and a Pt mesh counter electrode was used. The spectrum was measured with $^{20}Ne^+$ accelerated at 5 keV.

IV. Experiments

For the experiments with the tin (Sn) and platinum (Pt) as WEs, a 3-electrode setup was used. A platinum mesh was used as CE and an Ag/AgCl (saturated KCl) as RE. The Sn WE had an geometrical surface area of 3.5 cm^2 and the Pt mesh WE was 5x5 cm^2. Both experiments were performed in an H-cell with a 2.5 wt% gluconic acid solution with an electrolyte concentration of 1.5 wt%. The pH was set to 2.5. The reaction time of both experiments was 8 hours. For the experiment with the Sn WE, the potential was set to −1.16 V *vs.* RHE and for the Pt experiment the potential was −1.06 V *vs.* RHE. The values and the results are listed in Table S2.

Table S2: Summary of the experiments with the initial (c_0) and measured concentrations (c) of gluconic acid, glucose and the calculated produced glucose and the conversion rate (CR). The reaction time (t) was 8 h. The experiments were performed in an H-cell. A 3.5 cm^2 tin (Sn) wire and a platinum (Pt) mesh (5x5 cm^2) were used as WE, a platinum mesh as CE and an Ag/AgCl (saturated KCl) as RE. All reactions were performed in a solution with 2.5 wt% gluconic acid and 1.5 wt% $MgSO_4$ as electrolyte at a pH of 2.5.

WE	E / V vs RHE	c_0(Gluconic acid) / mmol L^{-1}	c_0(Glucose) / mmol L^{-1}	c(Gluconic acid) / mmol L^{-1}	c(Glucose) / mmol L^{-1}	$c(Glucose)_{prod.}$ / mmol L^{-1}	CR(Gluconic acid) / %
Sn	−1.16	128.56	0.120	128.85	0.141	0.020	0.016
Pt	−1.06	127.65	0.123	133.17	0.162	0.033	0.025

The experiments showed that with Sn and Pt as WEs, the glucose concentration was less than for the Ag experiments. The produced amount of glucose on the Ag WE was approximately 15 times higher than with Sn as WE. This is in contrast to the electrochemical reduction of CO_2 to CO and formic acid, where Sn is reported as one of the most active materials.[1] For the electrochemical reduction of gluconic acid to glucose on Ag, the conversion was 9 times higher than with Pt as electrocatalytic material. Therefore, the Ag WE was chosen as the preferred electrocatalytic material.

Reference

[1] Y. Chen, M. W. Kanan, *J. Am. Chem. Soc.*, 2012, **134**, 1986–1989.