The effect of methanol-water interaction on surface layer on titanium in CH_3OH-H_2O-$LiClO_4$ solutions

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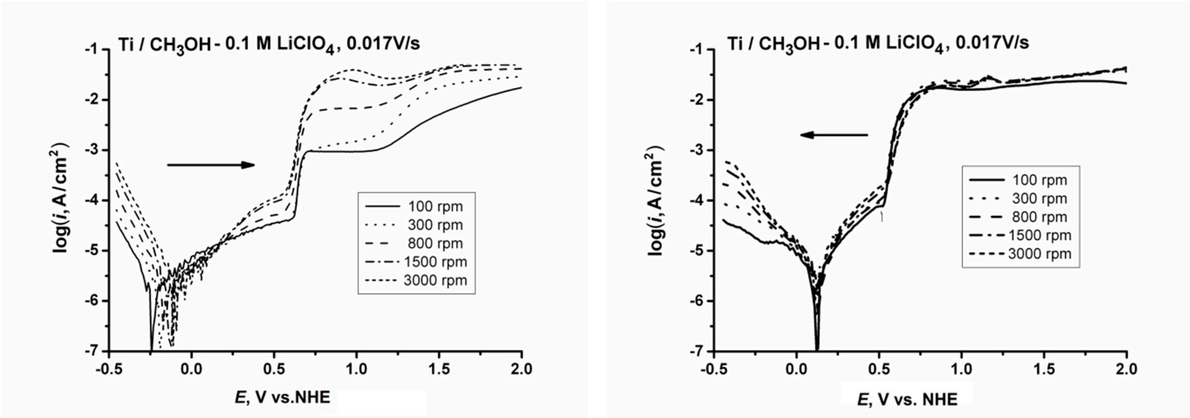


(a) (b)

Figure. S1 Effect of RDE rotation rate on polarization of Ti in CH_3OH – 0.1M $LiClO_4$ (v = 0.17 V/s), (a) scan in anodic direction, (b) reverse scan.

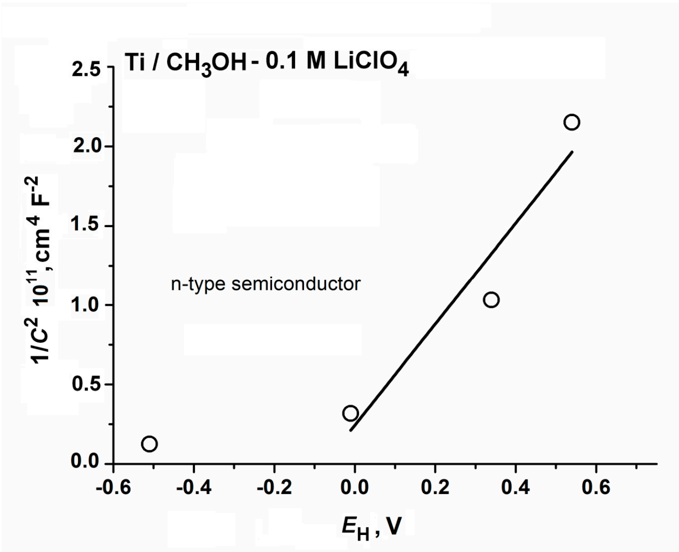
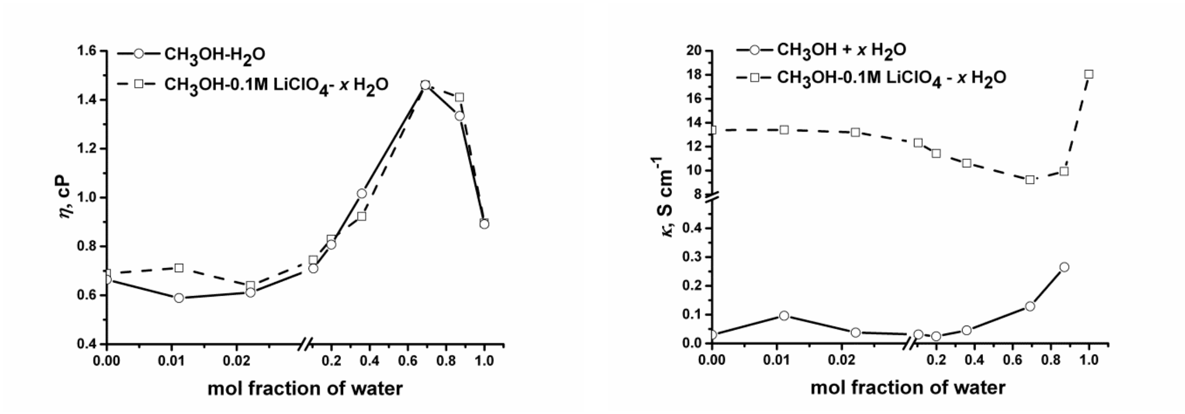
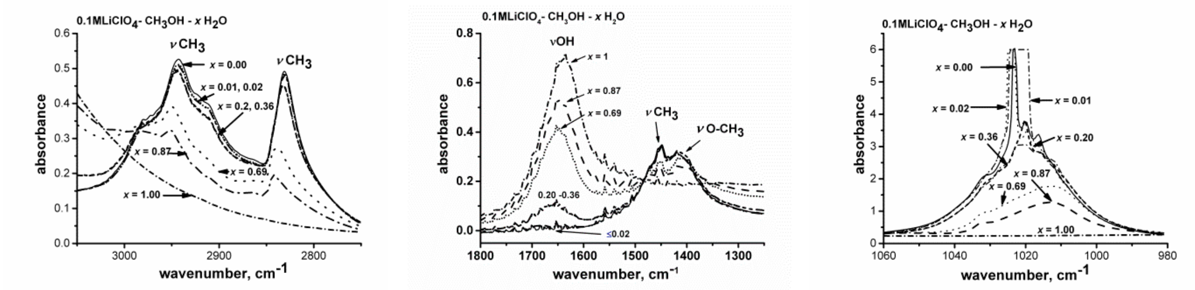


Figure. S2 Mott-Schottky diagram for Ti polarized in anhydrous CH_3OH-0.1 M $LiClO_4$.



(a) (b)

Figure.S3. Effect of water content on viscosity (a) and conductivity of CH_3OH-electrolyte-H_2O solutions.



(a) (b) (c)

Figure.S4. Effect of water content on the FTIR spectrum of CH_3OH-x H_2O-0.1M $LiClO_4$ solutions

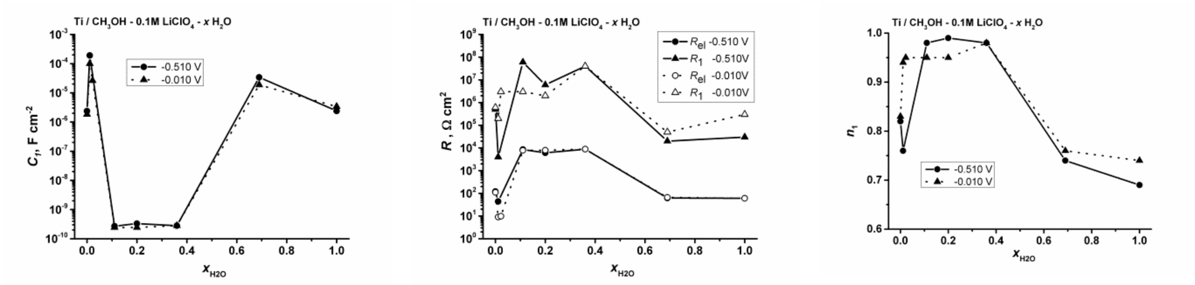


Figure. S5. Effect of water concentration on parameters of $R_{el}(Q_1R_1)$ element of equivalent circuit of impedance spectrum of titanium in CH_3OH-H_2O-0.1M $LiClO_4$

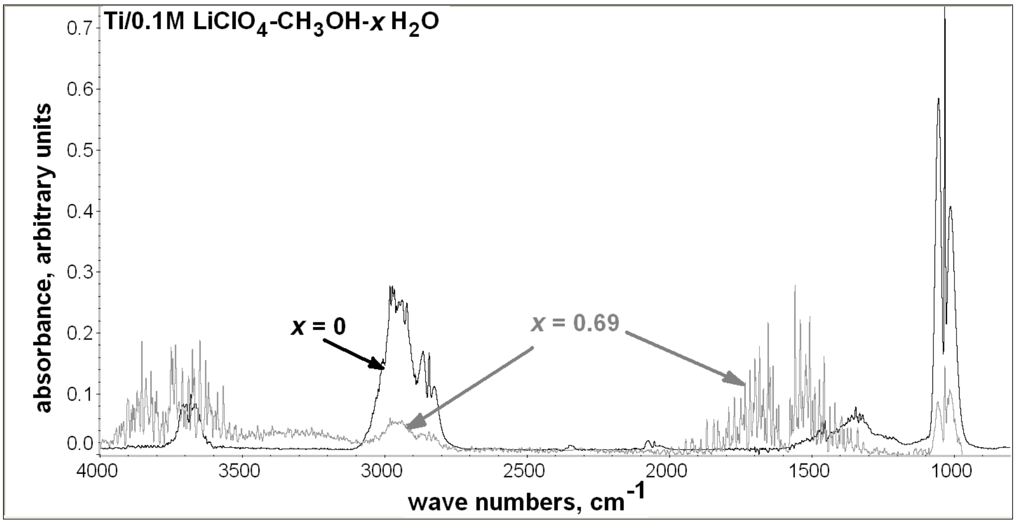


Figure. S6. FTIR-ATR spectra of layer formed on Ti in the pseudo-passive range in CH_3OH-0.1 M $LiClO_4$-H_2O solutions.

Table S1 Parameters of equivalent circuit $R_{el}(Q_1R_1(Q_2R_2))$ calculated for impedance spectra presented in Figure 3.

E_H V	R_{el}, Ω cm²	R_1 Ω cm²	Q_1 Fs^{n-1} cm^{-2}	n_1	R_2 Ω cm²	Q_2 Fs^{n-1} cm^{-2}	n_2
-0.510	116 ±4%	5.7E5 ±2%	9.5E-6 ±10%	0.79 ±2%	113 ±66%	9.2E-7 ±104%	0.56 ±2%
-0.010	124 ±4%	6.3E5 ±7%	6.5E-6 ±5%	0.87 ±1%	4.4E5 ±48%	2.6E-6 ±22%	0.59 ±2%
0.340	119 ±4%	8.4E5 ±68%	5.0E-6 ±7%	0.87 ±1%	2.4E5 ±86%	4.82E-6 ±32%	0.58 ±58%
0.540	120 ±8%	7.0E5 ±2%	3,5E-6 7%	0.90 ±2%	2,6E5 ±46%	3.6E-6 ±21%	0.60±21%

Table S2. Interpretation of XPS spectra for Ti surface etched potentiostatically in anhydrous CH_3OH-0.1M $LiClO_4$ at the prepassive range (-0.3 V vs. NHE, 90 min), passive range (0.125 V vs. NHE, 60 min) and transpassive range (0.6 V vs. NHE, 2 min).

etching potential	range	E_B, eV	%conc.	interpretation	Ref.
-0.3	C1s	285.3	33.84	C-C, C-H	[67-69]
		286.7	20.37	C-O	[70]
		289.1	6.59	C=O	[70]
	O1s	530.5	4.06	O-Ti	[70,71]
		532.6	16.10	M-OCH3	[70,71]
		533.4	17.17	O=C	[72]
	Ti2p	454.1	0.11	Ti(0)	[68,70]
		455.3	0.10	Ti(II)	[68,70]
		456.7	0.14	Ti(III)	[68,70]
		459.0	1.51	Ti(IV)	[68,70]
0.125	C1s	285.2	17.78	C-C, C-H	[67-69]
		286.1	13.98	C-O	[70]
		289.1	3.07	C=O	[70]
	O1s	530.5	27.80	O-Ti	[70,71]
		531.8	20.14	M-OCH3	[70,71]
		533.6	6.00	O=C	[72]
	Ti2p	453.9	0.15	Ti(0)	[68,70]
		454.7	0.67	Ti(II)	[68,70]
		457.4	1.88	Ti(III)	[68,70]
		459.0	8.53	Ti(IV)	[68,70]
0.6	C1s	285.2	17.78	C-C, C-H	[67-69]
		286.4	13.98	C-O	[70]
		289.2	3.07	C=O	[70]
	O1s	530.6	27.80	O-Ti	[70,71]
		532.1	20.14	M-OCH3	[70,71]
		533.0	6.00	O=C	[72]
	Ti2p	454.3	0.15	Ti(0)	[68,70]
		455.6	0.67	Ti(II)	[68,70]
		457.2	1.88	Ti(III)	[68,70]
		459.1	8.53	Ti(IV)	[68,70]

Table S3. Parameters of equivalent circuits $R_{el}(Q_1R_1)$ and $R_{el}(Q_1R_1(Q_2R_2))$ calculated for impedance spectra of Ti in CH_3OH-H_2O-0.1M $LiClO_4$ solutions at potentials of -0.0510 V and -0.010 V.

Molar fraction of water	R_{el} **Ω cm²**	Q_1 **Fs^{n-1}cm^{-2}**	n_1	R_1 **Ω cm²**	Q_2 **Fs^{n-1}cm^{-2}**	n_2	R_2 **Ω cm²**
-0.0510 V							
0	121	1.03E-5	0.82	5E+5	-	-	-
0.01	44	6.0E-4	0.76	4E+3	-	-	-
0.1	8575	3.50E-10	0.98	6E+7	2.03E-7	0.31	1E+6
0.2	6111	3.77E-10	0.99	6E+6	1.47E-7	0.57	3E+7
0.36	8855	3.63E-10	0.98	4E+7	6.73E-8	0.39	4E+6
0.69	62	1.69E-4	0.74	2E+4	-	-	-
1	61	3.70E-5	0.74	3E+4	-	-	-
-0.010 V							
0	110	7.78E-6	0.83	6E+5	-	-	-
0.01	9.1	1.53E-4	0.94	2E+5	-	-	-
0.02	9.8	3.98E-5	0.95	3E+6	-	-	-
0.11	7836	4.70E-10	0.95	3E+6	1.37E-7	0.42	2E+6
0.20	7874	4.72E-10	0.95	2E+6	8.75E-8	0.38	4E+6
0.36	8856	3.63E-10	0.98	4E+7	6.74E-8	0.39	4E+6
0.69	66	9.37E-5	0.76	5E+4	-	-	-
1	60	3.08E-5	0.74	3E+5	-	-	-

Table S4. Interpretation of band positions in FTIR-ATR spectrum of Ti surface in 0.1M $LiClO_4$-CH_3OH-xH_2O solution.

Wave number [cm^{-1}]	**Oscillation type**	**Type of bounding**	**Literature**
3700 -	O-H streching	alcohols	[56,57]
2800 - 3010	C-H stretching	CH_3, O-CH_3	[56,57]
1500 - 1600	O-H scissoring	OH in water	[56]
1300 - 1450	C-H scissoring	O-CH_3	[56,57]
1055	C-O stretching	alcohols	[56,57]
1006 - 1029	C-O stretching (deformation)	O-CH_3, (Ti-OCH_3)	[58-60]
665 - 680	C-H wagging	CH_3	[56,57]