Electronic Supplementary Material (ESI) for RSC Advances.

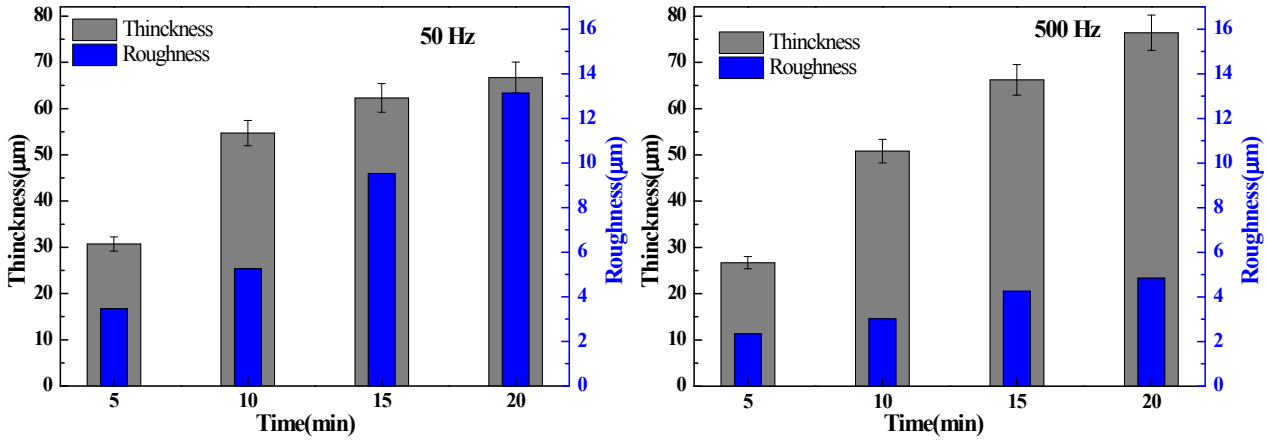
Supporting information

for

Study on coating growth characteristics during the electrolytic oxidation of magnesium-lithium alloy by optical emission spectroscopy analysis

Zhongping Yao, Qixing Xia, Dongqi Li, Zhaohua Jiang

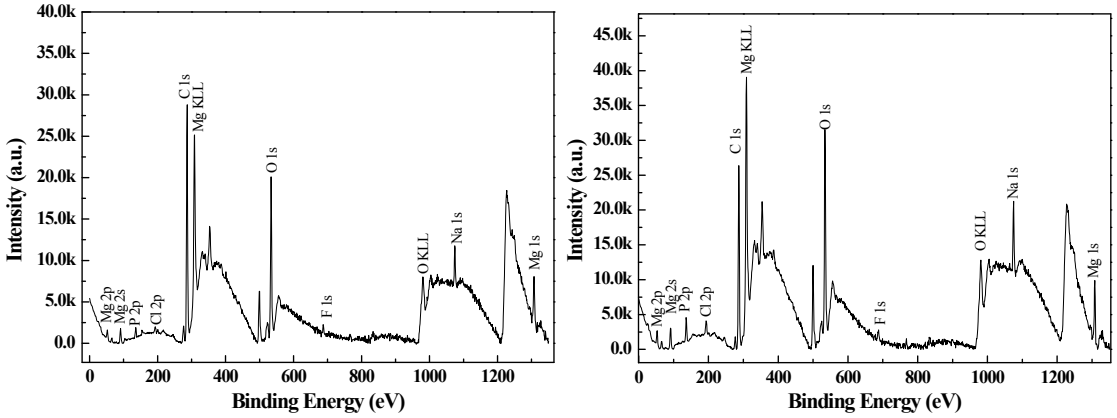
School of Chemical Engineering and Technology, State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150001 PR China



(a) 50 Hz (b) 500 Hz

SI Fig. 1 The roughness and thickness of the coatings prepared at 50 Hz and 500 Hz for different working times

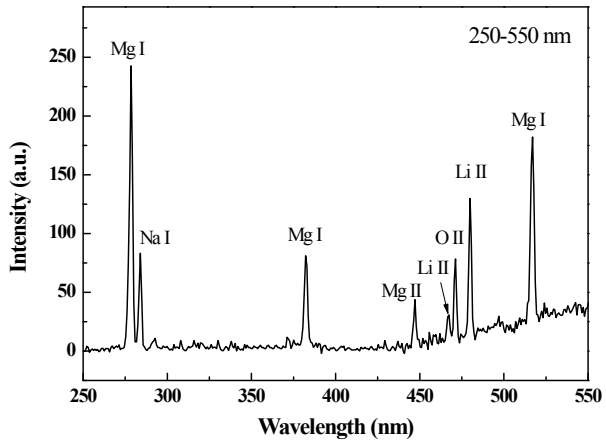
Notes: The thickness and roughness of the coatings at 50 Hz and 500 Hz increase by the working time extending. With higher roughness, the coatings prepared at 50 Hz have the similar thickness as that at 500 Hz until 15 min. When the working time to 20 min, the coatings prepared at 500 Hz is thicker about 15 μm than that at 50 Hz.



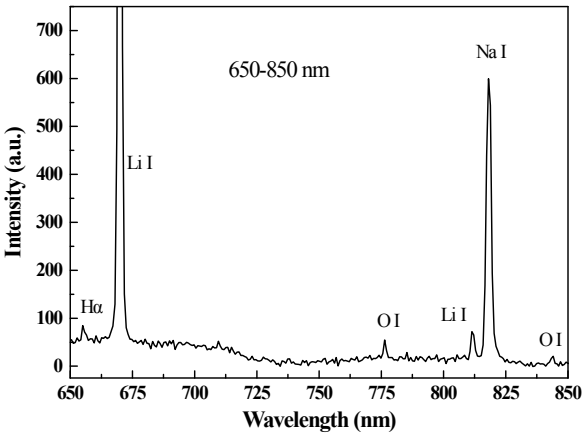
(a) 50 Hz (b) 500 Hz

SI Fig.2 The XPS spectrum of the PEO coatings prepared at (a) 50 Hz and (b) 500 Hz;

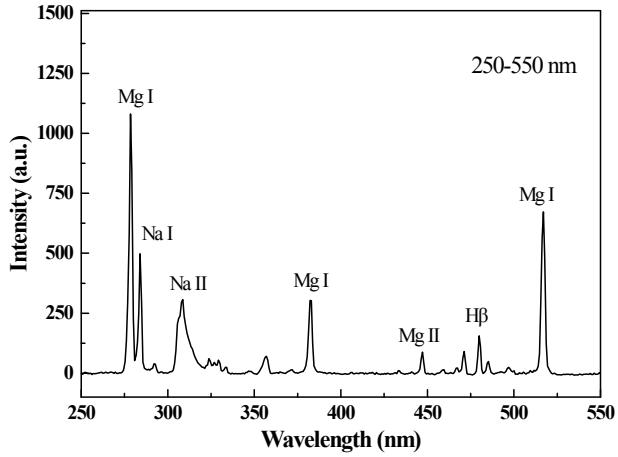
The XPS spectrums of the coatings prepared at 50 Hz are almost the same at that at 500 Hz. There are Mg 2p, Mg 2s, Mg KLL, Mg 1s, P 2p, O 1s, O KLL, F 1s and Na 1s from the substrate and electrolyte detected in the spectra. But C 1s and Cl 1s also emerged, which maybe come from the outer pollution.



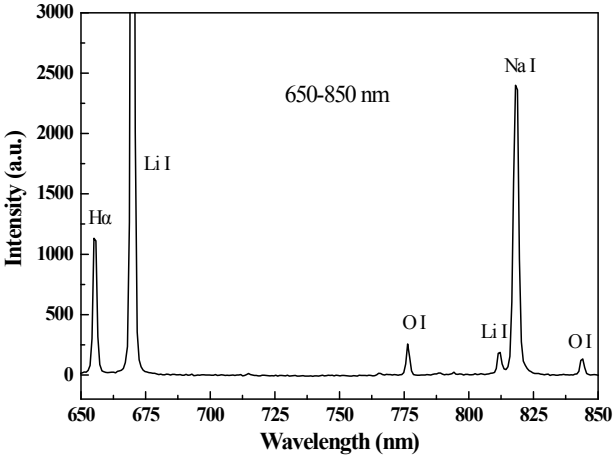
(a) 50 Hz, 250-550 nm



(b) 50 Hz, 650-850 nm



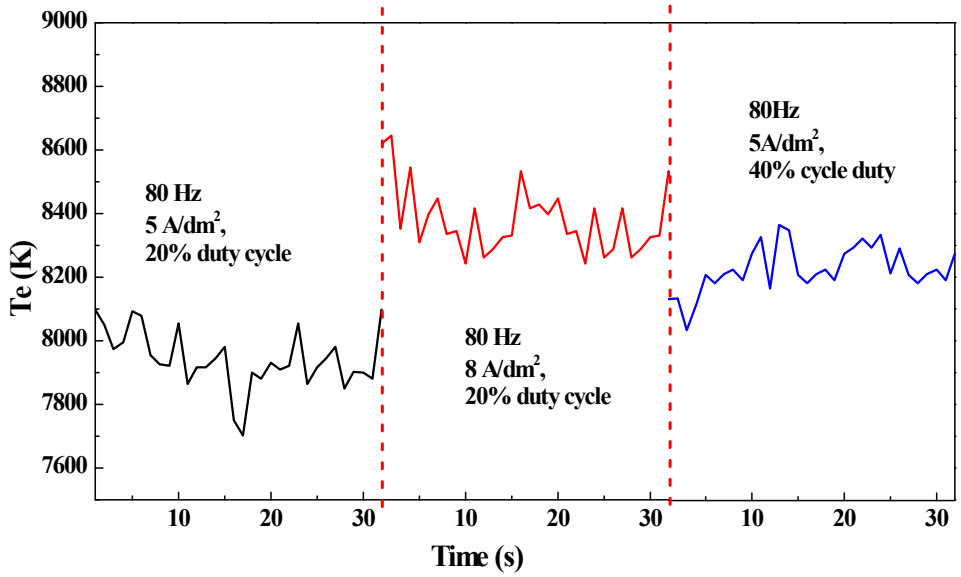
(c) 50 Hz, 250-550 nm



(d) 500 Hz, 650-850 nm

SI Fig. 3 The spectra fragments of 250-550 nm and 650-580 nm at 50 Hz and 500 Hz

Notes: The PEO spectroscopy are cut out two fragments of 250-550 nm and 650-580 nm. Except the lines of Li and Na, the emission lines of hydrogen α and β, oxygen and magnesium (Li and Mg from the substrate) are also detected in the spectra.



SI Fig. 4 Typical time variation of T_e by Na I lines in the PEO process in different current density and duty cycle at 80 Hz

Note: Form the SI Fig. 4, the T_e in the PEO process in 5 A/dm^2, 20% duty cycle at 80 Hz is 7900 ± 790 K. When the current density increase to 8 A/dm^2 or the duty cycle to 40%, the T_e change to 8400 ± 840 K or 8250 ± 825 K. These results shows that the T_e increases as the enhancing the current density and duty cycle.

SI Table 1 The relative contents (at. %) of the coatings prepared at different conditions by EDS analysis,

Frequency	Time	O K	F K	Na K	Mg K	PK
50 Hz	5 min	38.42	0.55	3.56	36.15	21.33
	10 min	38.95	0.67	3.89	35.2	21.29
	15 min	38.51	0.73	4.28	35.23	21.25
	20 min	39.42	1.02	4.83	34.82	19.91
500 Hz	5 min	37.55	0.43	4.38	35.3	22.34
	10 min	37.18	1.05	4.56	35.54	21.67
	15 min	37.83	0.29	3.85	36.19	21.84
	20 min	39.77	0.34	3.52	36.66	19.71

Notes: From the EDS analysis, it seems that all the coatings are composed of O, F, Na, Mg and P elements and the relative contents of the elements changes little with the PEO time and the working frequencies.

SI Table 2 The peaks emerged in PEO spectroscopy of SI Fig. 3 with the wavelength (λ), the transitions probabilities (A_{ki}), statistical weights of the upper states g_{k}。 (The notation I signify a neutral atom, while the II means the singly ionized atom)

Line	Λ, nm	A_{ki} (10^8S^{-1})	Transition	g_k	Energy (eV)
NaI	285.3	0.00554	$5p\ ^2P \rightarrow 3s\ ^2S$	4	4.345
NaI	589.0	0.614	$3p\ ^2P \rightarrow 3s\ ^2S$	4	2.104
NaI	819.5	0.54	$3d\ ^2D \rightarrow 3p\ ^2P$	6	3.617
NaII	309.3	-	$2p^5 3p\ ^3D \rightarrow 2p^5 3s\ ^3P$	7	4.008
LiI	610.4	0.686	$3d\ ^2D \rightarrow 2p\ ^2P$	6	2.031
LiI	670.8	0.369	$2p\ ^2P \rightarrow 2s\ ^2S$	2	1.848
LiI	812.6	0.349	$3s\ ^2S \rightarrow 2p\ ^2P$	2	1.525
MgI	278.0	3.92	$3p2\ ^3P \rightarrow 3s3p\ ^3P$	5	4.459
MgI	383.3	1.68	$3s3d\ ^3D \rightarrow 3s3p\ ^3P$	7	3.229
MgI	517.3	0.346	$3s4s\ ^3S \rightarrow 3s3p\ ^3P$	3	2.396
MgII	448.1	2.23	$4f\ ^2F \rightarrow 3d\ ^2D$	8	2.766
H_β	486.1	0.1719	$4d\ ^2D \rightarrow 2p\ 2P$	4	2.550
H_α	656.3	0.6465	$3d\ ^2D \rightarrow 2p\ ^2P$	6	1.889
OI	777.2	0.369	$2s^2 2p^3(^4S)3p\ ^5P \rightarrow 2s^2 2p^3(^4S)3s\ ^5S$	7	1.594
OI	844.6	0.322	$2s^2 2p^3(^4S)^3p\ ^3P \rightarrow 2s^2 2p^3(^4S)3s\ ^3S$	1	1.468

Notes: SI Table 2 is the main spectral lines observed in the spectroscopy with the wavelength. The PEO spectroscopy contains sodium, hydrogen α and β, oxygen (Na, H and O, from the electrolyte), lithium and magnesium (Li and Mg from the substrate). The related values of the Na I lines (589.0

nm and 819.5 nm) are used to calculate the T_e due to that the Na lines is the strongest in the PEO spectra.