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Supporting Information

The Electrochemical Behaviour of Magnetocaloric Alloys La(Fe,Mn,Si)$_{13}$H$_x$ under Magnetic Field Conditions

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Experimental

Material: Two La(Fe,Mn,Si)$_{13}$H$_x$ alloys, $LaFe_{11.22}Mn_{0.46}Si_{1.33}H_x$ ($LFMSH_1$) and $LaFe_{11.28}Mn_{0.40}Si_{1.32}H_x$ ($LFMSH_2$), were supplied by Camfridge Ltd. The samples for electrochemical tests were approximately square plates with a typical area size of ~0.2 cm^2.

Characterization: Characterization of the sample surface and EDX analysis of the compositions were carried out using a LEO Gemini 1525 FEGSEM. Magnetometry measurements were carried out using vibrating sample magnetometry in a Quantum Design Physical Property Measurement System (PPMS) with a 2 K to 400 K variable temperature cryostat and up to 9 T magnetic field available.[1]

Experimental set-up: The experimental set-up is shown in Supporting Information (Fig. S4, ESI†). In the test cell, positions of the as-received sample (working electrode, WE) and Pt foil (counter electrode, CE) were fixed by plastic screws so that they faced each other, to ensure the horizontal current flow between the WE and CE. Ag/AgCl/KCl (3 M) was used as the reference electrode. The cell was not sealed and all the electrochemistry tests were considered to be carried out under naturally-aerated conditions. The test cell was connected with a supporting rod, which fitted into an actuator (Model EZC6-30M, Oriental Motor Co. Ltd) to control the movement of the test cell. A permanent magnet (Halbach cylinder) was used to study the effect of magnetic fields on the corrosion behaviour.

In the tests with a constant magnetic field, the sample was at the center of the magnet, where the field was 1.1 T. This position was noted as '1.1 T position' in this study. In the tests to study the effect of the direction of the magnetic field (parallel or perpendicular), the magnet was manually rotated 90° to change the direction of the field. In the tests without magnetic fields, the center of the sample was moved upward (in 1 s) by the actuator and away from the center of the magnet to a position where the magnetic field was negligible (in the context of the magnetocaloric effect, < 0.01 T). This position was referred to as 'zero position'. Under a changing magnetic field, the sample was moved between 'zero position' and '1.1 T position' in 1 s continuously, *i.e.*, the frequency of the upward/ downward movement was 1 Hz. This will be referred as 'changing field' in the current study. Dummy tests with a sample moving upward and downward at 1 Hz, but without a magnetic field, were carried out to investigate the effect of linear movements (*i.e*. did physical movement of the cell cause sufficient disruption to the electrolyte to affect the corrosion behaviour?).

Electrochemical procedure: In the potentiodynamic tests, the sample was anodically polarized at a sweep rate of 0.5 mV s^{-1} from cathodic region until the current reached the set-point value 1 mA cm^{-2} after immersion in solution for 3600 s at open circuit potential (OCP). In the potentiostatic tests, various potentials, determined from preliminary dynamic polarisation data, were applied to the samples with/without magnetic fields after initial immersion in solution for 600 s at OCP. All electrochemical tests were carried out in 0.1 M $NaClO_4$ as a non-interacting supporting electrolyte using ACM Instrument Gill AC potentiostats.

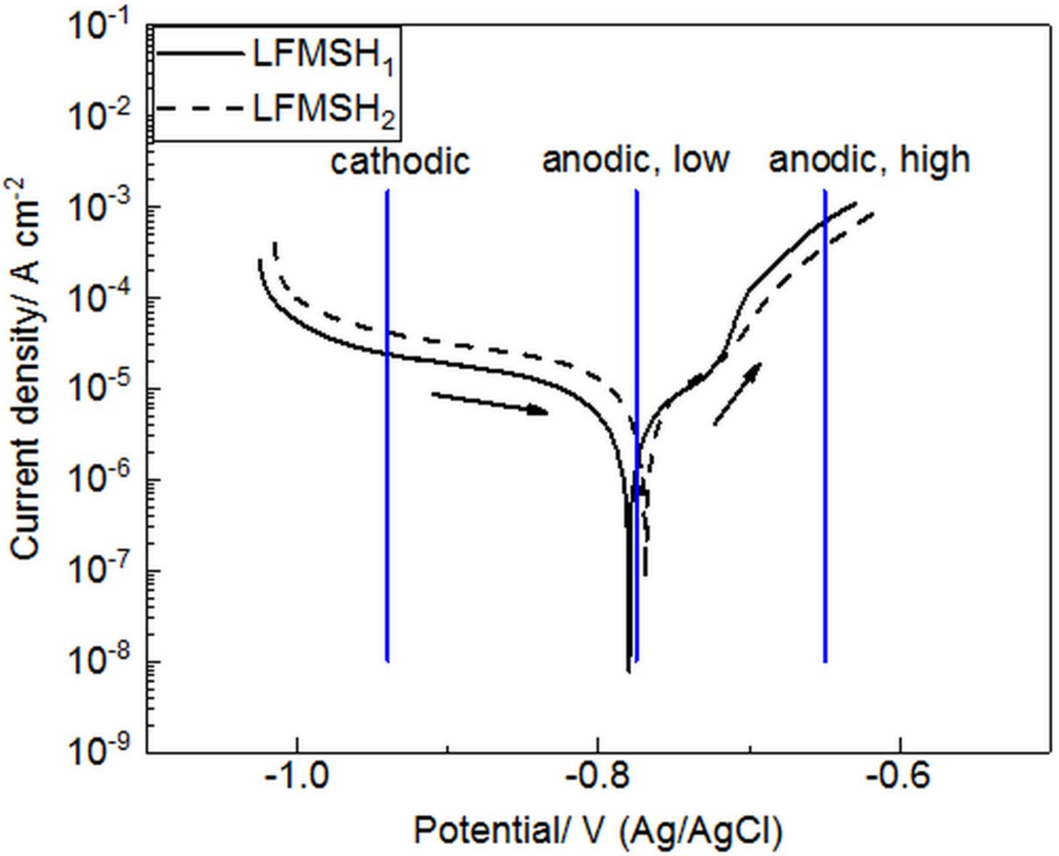

Figure S1. Linear polarisation sweep of LFMSH$_1$ and LFMSH$_2$ samples from cathodic to anodic region at 0.5 mV s^{-1} after immersion in solution for 3600 s at OCP. Tests were carried out in naturally-aerated 0.1 M NaClO$_4$ solutions at room temperature without magnetic fields. The vertical lines indicate the potential to be applied for LFMSH$_1$ in the potentiostatic tests.

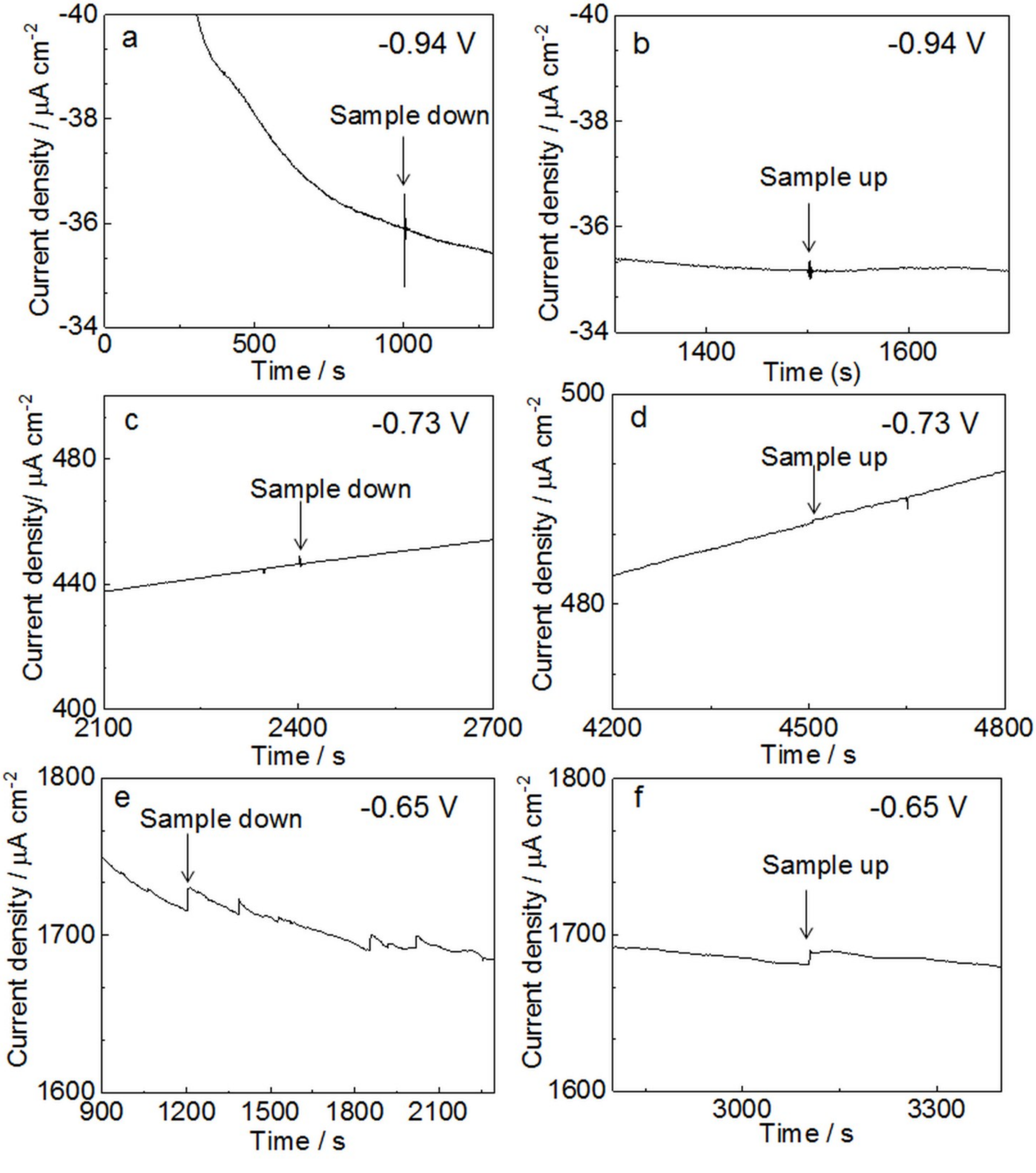

Figure S2. The sample (LFMSH$_1$) was held at (a) and (b) -0.94 V for 4800 s, (c) and (d) -0.73 V for 5000 s, -0.6 V for 2400 s and (e) and (f) -0.65 V after immersion in solution for 3600 s at OCP. The sample was moved (a), (c) and (e) downwards from 'zero position' to '1.1 T position' and (b), (d) and (f) upwards from '1.1 T position' to 'zero position'. The movements were completed in 1 s. Tests were carried out in naturally-aerated 0.1 M NaClO$_4$ at room temperature without magnetic fields.

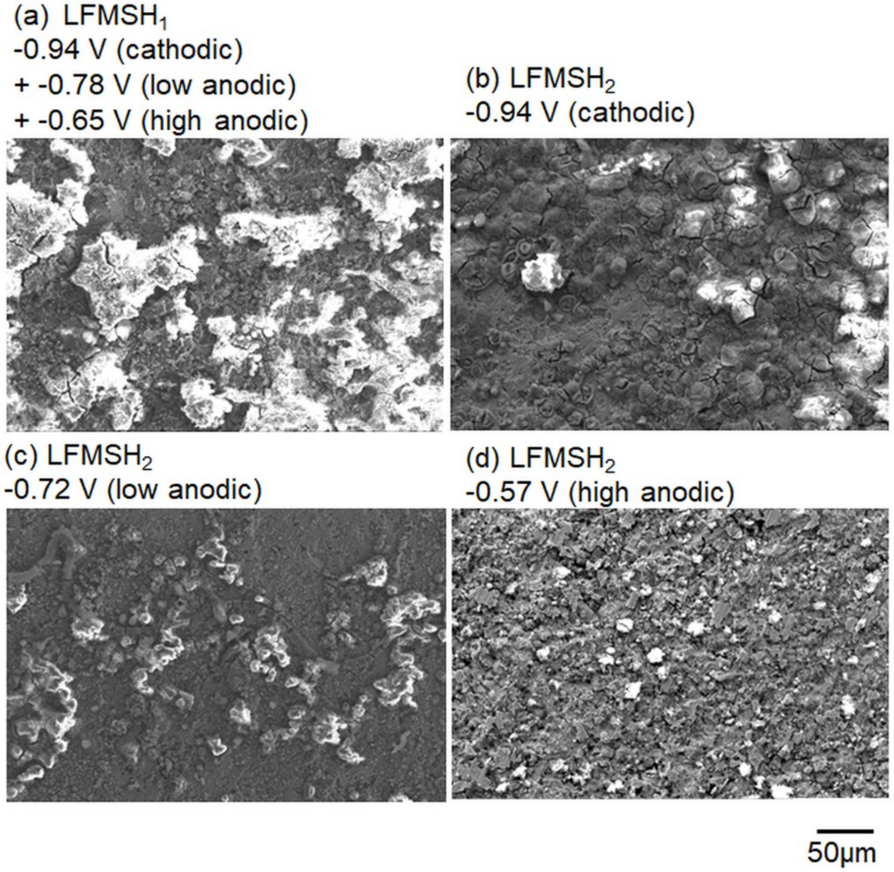

Figure S3. SEM images of the LFMSH$_1$ and LFMSH$_2$ samples after applied with the potentials (or series of potential steps) indicated in the figure.

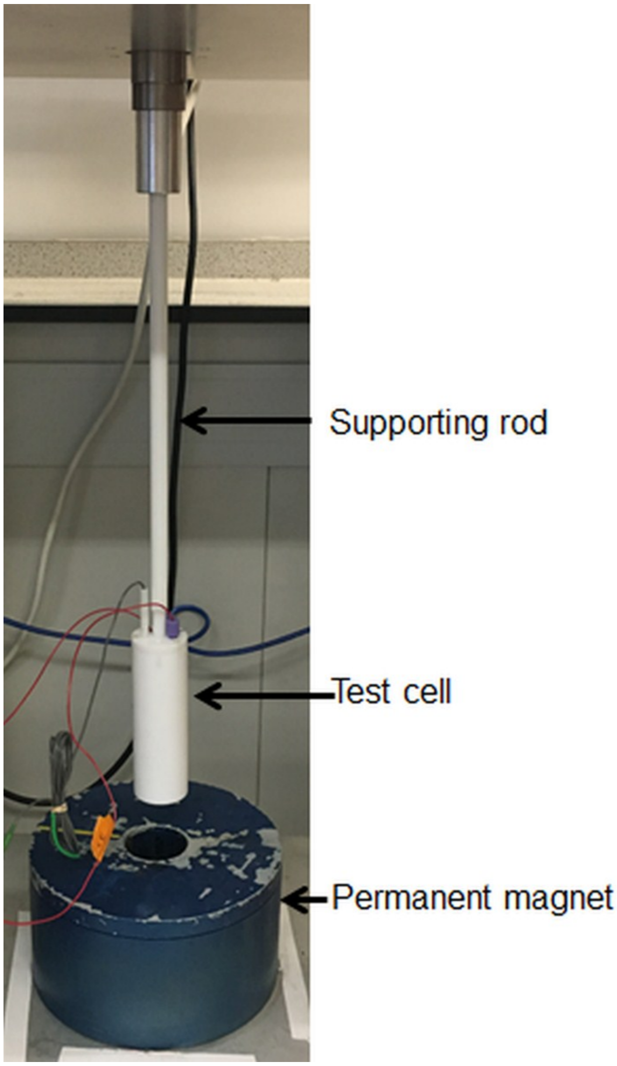

Figure S4. Experimental set-up of electrochemical tests.

Table S1. Summary of *maximum* current densities changes observed during stepping the magnetic field between 'no field' position to either parallel or perpendicular field. Noted are the current densities directly before and after the field change (shown in Figure 3), with the difference in percentage shown in brackets. '*' indicates that this maximum change was observed from the 'field on' to 'no field' position.

	No field to a parallel field [μA cm^{-2}]	No field to a perpendicular field [μA cm^{-2}]
Paramagnetic - cathodic	49 to 75 (+53%)	48 to 48 (0)
Paramagnetic - low anodic	25 to 20 (-20%)	22 to 23 (+4%)*
Paramagnetic – high anodic	1718 to 1825 (+6%)	1583 to 1587 (+1%)
Ferromagnetic – cathodic	48 to 30 (-38%)*	36 to 34 (-5%)
Ferromagnetic – low anodic	96 to 90 (-6%)*	81 to 72 (-11%)*
Ferromagnetic – high anodic	1835 to 1939 (+6%)	2999 to 3023 (+1%)

Table S2. EDX analysis of three phases (one α-Fe phase, one La-rich phase, and the matrix) in as-received LFMSH$_1$ and LFMSH$_2$ samples.

weight%		O	Si	Mn	Fe	La
LFMSH$_1$	α-Fe	0	1.3	2.9	95.3	0.5
	La rich	18.0	0.6	0	30.1	51.3
	matrix	0	4.7	1.8	76.2	17.3
LFMSH$_2$	α-Fe	0	1.1	2.7	95.6	0.6
	La rich	16.8	0.6	0	11.9	70.7
	matrix	0	4.9	1.8	74.9	18.4

Table S3. EDX analysis of $LFMSH_1$ and $LFMSH_2$ samples after corrosion tests shown in Figures 3(b), (d), (e) and (f).

Weight%		O	Si	Mn	Fe	La
$LFMSH_1$	After -0.94 V (cathodic), -0.78 V (low anodic) and -0.65 V (high anodic)	33.5	3.8	1.5	46.8	14.4
$LFMSH_2$	After -0.94 V (cathodic)	26.4	0.5	1.7	50.3	21.1
	After -0.72 V (low anodic)	22.8	2.2	1.5	57.0	16.5
	After -0.57 V (high anodic)	12.4	7.5	1.7	66.2	12.2

References:

1. M. Bratko, E. Lovell, A. D. Caplin, V. Basso, A. Barcza, M. Katter and L. F. Cohen, *Phys. Rev. B*, 2017, **95**, 064411.