

# Corrosion Protection Characteristics of Doped Magnetite Layers on Carbon Steel Surfaces in Aqueous CO<sub>2</sub> Environments

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## SUPPLEMENARTY MATERIAL

**Figure S1** shows cyclic voltammetry measurements on a gold electrode in a 2 M NaOH, 1 M TEA solution at 80 °C containing mixed metal sulphates.

**Figure S2** shows potentiodynamic polarisation measurements on bare carbon steel and layered carbon steel surfaces performed in a 50 °C, pH 5, 1 wt.% NaCl solution.

**Figure S3** shows Bode plots measured on bare carbon steel and layered carbon steel surfaces performed in a 50 °C, pH 5, 1 wt.% NaCl solution.

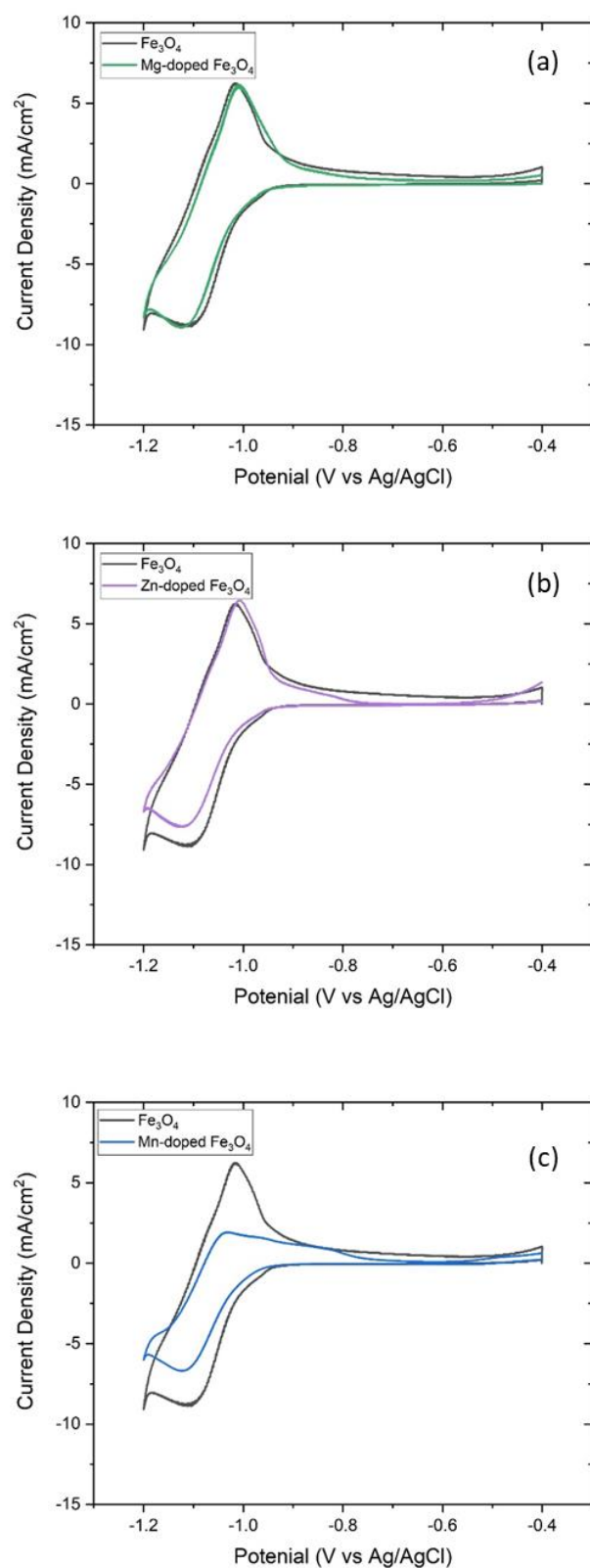
**Table S1** shows electrical equivalent circuit behaviour measured on bare carbon steel in a 50 °C, pH 5, 1 wt.% NaCl solution over 24 h.

**Table S2** shows electrical equivalent circuit behaviour measured on carbon steel with an Fe<sub>3</sub>O<sub>4</sub> layer in a 50 °C, pH 5, 1 wt.% NaCl solution over 24 h.

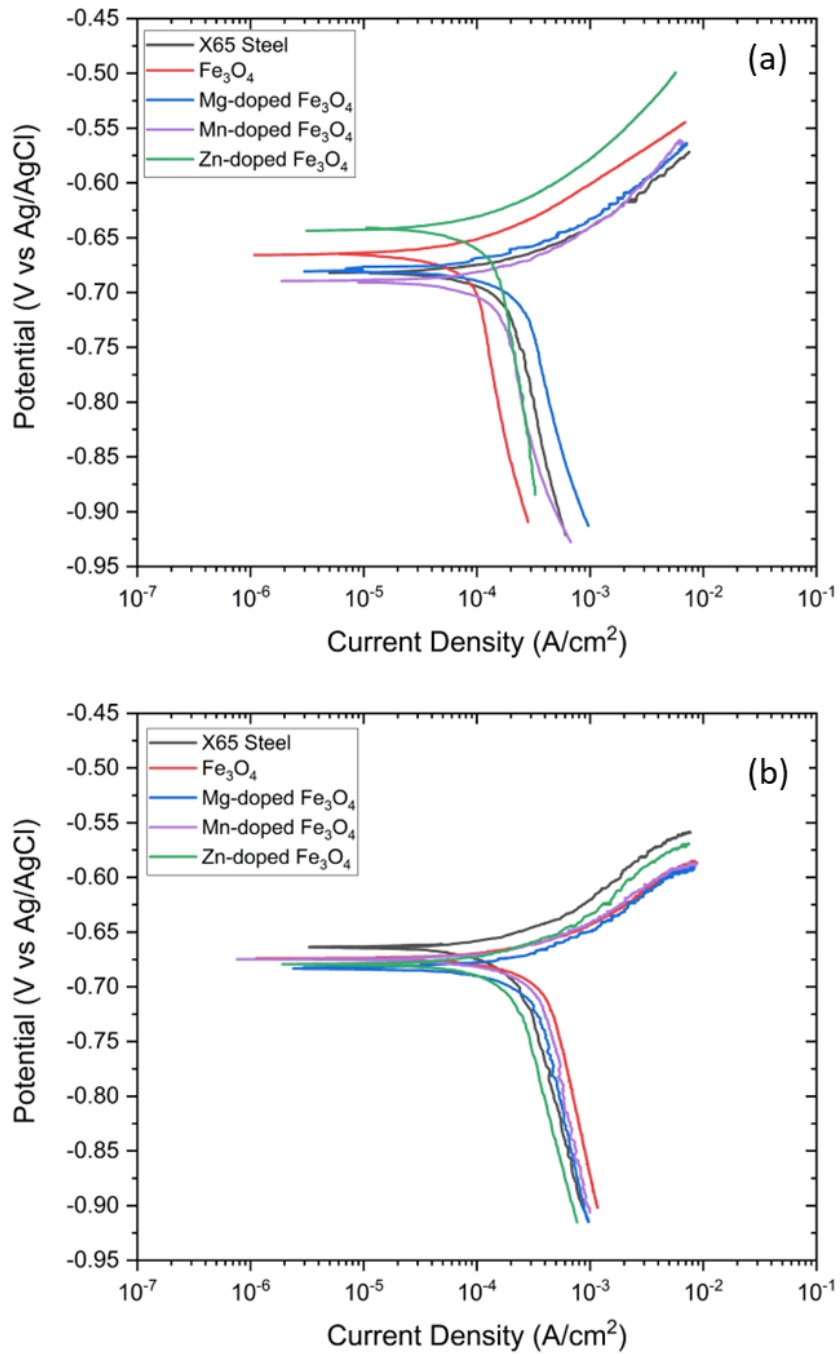
**Table S3** shows electrical equivalent circuit behaviour measured on carbon steel with a Mg-doped Fe<sub>3</sub>O<sub>4</sub> layer in a 50 °C, pH 5, 1 wt.% NaCl solution over 24 h.

**Table S4** shows electrical equivalent circuit behaviour measured on carbon steel with a Mn-doped Fe<sub>3</sub>O<sub>4</sub> layer in a 50 °C, pH 5, 1 wt.% NaCl solution over 24 h.

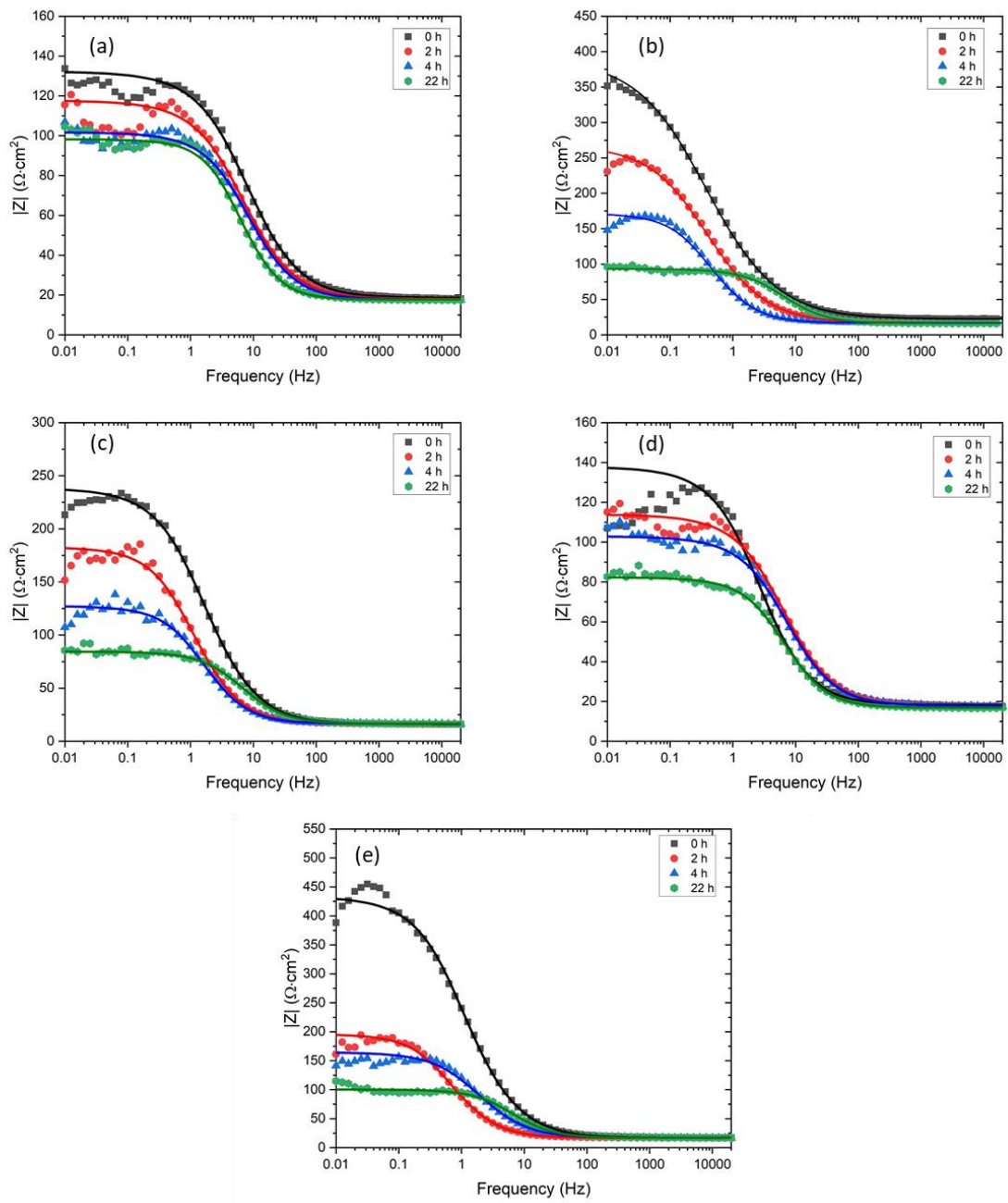
**Table S5** shows electrical equivalent circuit behaviour measured on carbon steel with a Zn-doped Fe<sub>3</sub>O<sub>4</sub> layer in a 50 °C, pH 5, 1 wt.% NaCl solution over 24 h.



**Figure S1:** Cyclic voltammograms on a 0.02 cm<sup>2</sup> Au electrode measured at a scan rate of 50 mV/s in an unstirred 2 M NaOH, 1 M TEA solution at 80 °C containing 0.032 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and (a) 0.011 M MgSO<sub>4</sub>, (b) 0.011 M ZnSO<sub>4</sub> (c) 0.011 M MnSO<sub>4</sub> and compared with a solution containing 0.043 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> without the addition of other metal sulphates (black lines)



**Figure S2:** Potentiodynamic polarisation resistance plots measured after (a) 4 h and (b) 24 h of exposure to a 50 °C, pH 5, 1 wt.% NaCl solution for bare X65 carbon steel, Fe<sub>3</sub>O<sub>4</sub>-layered X65, Mg-doped Fe<sub>3</sub>O<sub>4</sub>-layered X65, Mn-doped Fe<sub>3</sub>O<sub>4</sub>-layered X65 and Zn-doped Fe<sub>3</sub>O<sub>4</sub>-layered X65 coupons.



**Figure S3:** Bode magnitude plots from EIS measurements performed in a 50 °C, pH 5, 1 wt.% NaCl solution on (a) bare X65 carbon steel, (b)  $\text{Fe}_3\text{O}_4$ -layered X65, (c) Mg-doped  $\text{Fe}_3\text{O}_4$ -layered X65, (d) Mn-doped  $\text{Fe}_3\text{O}_4$ -layered X65 and (e) Zn-doped  $\text{Fe}_3\text{O}_4$ -layered X65 coupons

**Table S1:** Fitting parameters obtained using a simplified Randle's circuit for the data obtained and calculated for X65 carbon steel

| Time (h) | $R_e$ ( $\Omega \cdot \text{cm}^2$ ) | $R_{ct}$ ( $\Omega \cdot \text{cm}^2$ ) | $R_{ct}$ Error ( $\Omega \cdot \text{cm}^2$ ) | $Q_{dl}$ ( $\mu\text{F}/\text{cm}^2$ ) $^\alpha$ | $Q_{dl}$ Error ( $\mu\text{F}/\text{cm}^2$ ) $^\alpha$ | $\alpha$ | $C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ ) | $R_{ct} \cdot C_{dl}$ |
|----------|--------------------------------------|---|---|--|--|----------|--|-----------------------|
| 0        | 18.6                                 | 114                                     | 1.1   | 564  | 16   | 0.77     | 138                                    | 0.016                 |
| 2        | 18.0                                 | 100                                     | 1.1   | 689  | 23   | 0.78     | 191                                    | 0.019                 |
| 4        | 17.7                                 | 84                                      | 0.7   | 612  | 21   | 0.82     | 213                                    | 0.018                 |
| 6        | 17.6                                 | 82                                      | 0.6   | 575  | 16   | 0.83     | 220                                    | 0.018                 |
| 8        | 17.4                                 | 82                                      | 0.6   | 541  | 16   | 0.85     | 227                                    | 0.019                 |
| 10       | 17.5                                 | 83                                      | 0.6   | 578  | 11   | 0.84     | 235                                    | 0.020                 |
| 12       | 17.5                                 | 80                                      | 0.6   | 535  | 16   | 0.87     | 257                                    | 0.021                 |
| 14       | 17.5                                 | 79                                      | 0.6   | 548  | 17   | 0.87     | 274                                    | 0.022                 |
| 16       | 17.5                                 | 80                                      | 0.5   | 597  | 14   | 0.87     | 291                                    | 0.023                 |
| 18       | 17.5                                 | 79                                      | 0.5   | 577  | 16   | 0.89     | 312                                    | 0.025                 |
| 20       | 17.3                                 | 82                                      | 0.6   | 605  | 18   | 0.89     | 333                                    | 0.027                 |
| 22       | 17.7                                 | 81                                      | 0.6   | 631  | 18   | 0.89     | 358                                    | 0.029                 |

**Table S2:** Fitting parameters obtained using a simplified Randle's circuit for the data obtained and calculated for X65 carbon steel with an  $\text{Fe}_3\text{O}_4$  layer

| Time (h) | $R_e$ ( $\Omega \cdot \text{cm}^2$ ) | $R_{ct}$ ( $\Omega \cdot \text{cm}^2$ ) | $R_{ct}$ Error ( $\Omega \cdot \text{cm}^2$ ) | $Q_{dl}$ ( $\mu\text{F}/\text{cm}^2$ ) $^\alpha$ | $Q_{dl}$ Error ( $\mu\text{F}/\text{cm}^2$ ) $^\alpha$ | $\alpha$ | $C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ ) | $R_{ct} \cdot C_{dl}$ |
|----------|--------------------------------------|---|---|--|--|----------|--|-----------------------|
| 0        | 22.2                                 | 370                                     | 3.3   | 1943   | 24   | 0.65     | 337                                    | 0.125                 |
| 2        | 17.0                                 | 251                                     | 2.2   | 2733   | 35   | 0.73     | 845                                    | 0.212                 |
| 4        | 17.0                                 | 155                                     | 1.6   | 3687   | 62   | 0.86     | 2266                                   | 0.351                 |
| 6        | 16.8                                 | 120                                     | 1.2   | 4433   | 62   | 0.89     | 3202                                   | 0.383                 |
| 8        | 17.1                                 | 107                                     | 1.6   | 3891   | 81   | 0.90     | 2808                                   | 0.300                 |
| 10       | 16.9                                 | 106                                     | 2.4   | 3020   | 111  | 0.74     | 1005                                   | 0.107                 |
| 12       | 16.6                                 | 97                                      | 0.9   | 878  | 20   | 0.82     | 330                                    | 0.032                 |
| 14       | 16.7                                 | 91                                      | 0.8   | 684  | 15   | 0.84     | 287                                    | 0.026                 |
| 16       | 16.9                                 | 91                                      | 0.8   | 640  | 17   | 0.86     | 289                                    | 0.026                 |
| 18       | 15.7                                 | 87                                      | 0.8   | 652  | 15   | 0.86     | 297                                    | 0.026                 |
| 20       | 16.4                                 | 86                                      | 0.7   | 637  | 18   | 0.87     | 315                                    | 0.027                 |
| 22       | 16.3                                 | 77                                      | 0.5   | 739  | 13   | 0.85     | 333                                    | 0.026                 |

**Table S3:** Fitting parameters obtained using a simplified Randle's circuit for the data obtained and calculated for X65 carbon steel with a Mg-doped Fe<sub>3</sub>O<sub>4</sub> layer

| Time (h) | R <sub>e</sub> (Ω.cm <sup>2</sup> ) | R <sub>ct</sub> (Ω.cm <sup>2</sup> ) | R <sub>ct</sub> Error (Ω.cm <sup>2</sup> ) | Q <sub>dl</sub> (μF/cm <sup>2</sup> ) <sup>α</sup> | Q <sub>dl</sub> Error (μF/cm <sup>2</sup> ) <sup>α</sup> | α    | C <sub>dl</sub> (μF/cm <sup>2</sup> ) | R <sub>ct</sub> .C <sub>dl</sub> |
|----------|-------------------------------------|--------------------------------------|--|--|--|------|---------------------------------------|----------------------------------|
| 0        | 16.2                                | 222                                  | 0.8  | 947  | 8  | 0.79 | 311                                   | 0.069                            |
| 2        | 16.5                                | 167                                  | 1.4  | 1591   | 27   | 0.84 | 786                                   | 0.131                            |
| 4        | 16.6                                | 111                                  | 1.0  | 1677   | 29   | 0.86 | 897                                   | 0.099                            |
| 6        | 16.6                                | 98                                   | 0.8  | 855  | 19   | 0.80 | 279                                   | 0.027                            |
| 8        | 16.7                                | 97                                   | 0.6  | 787  | 15   | 0.79 | 236                                   | 0.023                            |
| 10       | 16.6                                | 83                                   | 0.4  | 693  | 10   | 0.82 | 242                                   | 0.020                            |
| 12       | 17.0                                | 85                                   | 0.5  | 674  | 13   | 0.83 | 257                                   | 0.022                            |
| 14       | 17.0                                | 75                                   | 0.5  | 681  | 15   | 0.85 | 292                                   | 0.022                            |
| 16       | 17.0                                | 75                                   | 0.4  | 683  | 15   | 0.85 | 292                                   | 0.022                            |
| 18       | 16.8                                | 70                                   | 0.4  | 699  | 17   | 0.85 | 314                                   | 0.022                            |
| 20       | 16.6                                | 70                                   | 0.4  | 757  | 16   | 0.85 | 335                                   | 0.023                            |
| 22       | 16.6                                | 68                                   | 0.3  | 813  | 14   | 0.85 | 359                                   | 0.024                            |

**Table S4:** Fitting parameters obtained using a simplified Randle's circuit for the data obtained and calculated for X65 carbon steel with a Mn-doped Fe<sub>3</sub>O<sub>4</sub> layer

| Time (h) | R <sub>e</sub> (Ω.cm <sup>2</sup> ) | R <sub>ct</sub> (Ω.cm <sup>2</sup> ) | R <sub>ct</sub> Error (Ω.cm <sup>2</sup> ) | Q <sub>dl</sub> (μF/cm <sup>2</sup> ) <sup>α</sup> | Q <sub>dl</sub> Error (μF/cm <sup>2</sup> ) <sup>α</sup> | α    | C <sub>dl</sub> (μF/cm <sup>2</sup> ) | R <sub>ct</sub> .C <sub>dl</sub> |
|----------|-------------------------------------|--------------------------------------|--|--|--|------|---------------------------------------|----------------------------------|
| 0        | 18.2                                | 120                                  | 1.5  | 1169   | 33   | 0.79 | 416                                   | 0.050                            |
| 2        | 17.7                                | 96                                   | 0.7  | 738  | 16   | 0.78 | 215                                   | 0.021                            |
| 4        | 17.7                                | 85                                   | 0.6  | 718  | 18   | 0.80 | 230                                   | 0.020                            |
| 6        | 17.4                                | 81                                   | 0.6  | 678  | 17   | 0.81 | 232                                   | 0.019                            |
| 8        | 17.3                                | 82                                   | 0.5  | 642  | 14   | 0.83 | 238                                   | 0.019                            |
| 10       | 17.2                                | 77                                   | 0.4  | 634  | 13   | 0.83 | 246                                   | 0.019                            |
| 12       | 17.5                                | 76                                   | 0.5  | 634  | 14   | 0.84 | 266                                   | 0.020                            |
| 14       | 17.4                                | 76                                   | 0.5  | 618  | 20   | 0.86 | 282                                   | 0.021                            |
| 16       | 16.7                                | 75                                   | 0.4  | 772  | 13   | 0.83 | 301                                   | 0.023                            |
| 18       | 17.1                                | 69                                   | 0.3  | 745  | 12   | 0.85 | 326                                   | 0.023                            |
| 20       | 16.7                                | 68                                   | 0.4  | 799  | 12   | 0.85 | 351                                   | 0.024                            |
| 22       | 16.8                                | 65                                   | 0.3  | 855  | 15   | 0.85 | 381                                   | 0.025                            |

**Table S5:** Fitting parameters obtained using a simplified Randle's circuit for the data obtained and calculated for X65 carbon steel with a Zn-doped Fe<sub>3</sub>O<sub>4</sub> layer

| Time (h) | R <sub>e</sub> (Ω.cm <sup>2</sup> ) | R <sub>ct</sub> (Ω.cm <sup>2</sup> ) | R <sub>ct</sub> Error (Ω.cm <sup>2</sup> ) | Q <sub>d1</sub> (μF/cm <sup>2</sup> ) <sup>α</sup> | Q <sub>d1</sub> Error (μF/cm <sup>2</sup> ) <sup>α</sup> | α    | C <sub>d1</sub> (μF/cm <sup>2</sup> ) | R <sub>ct</sub> .C <sub>d1</sub> |
|----------|-------------------------------------|--------------------------------------|--|--|--|------|---------------------------------------|----------------------------------|
| 0        | 17.3                                | 416                                  | 3.5  | 696  | 9  | 0.80 | 224                                   | 0.093                            |
| 2        | 17.0                                | 179                                  | 1.4  | 2182   | 28   | 0.86 | 1244                                  | 0.223                            |
| 4        | 17.2                                | 148                                  | 1.9  | 1213   | 30   | 0.81 | 489                                   | 0.072                            |
| 6        | 17.1                                | 105                                  | 0.9  | 698  | 18   | 0.81 | 239                                   | 0.025                            |
| 8        | 17.2                                | 98                                   | 0.7  | 690  | 17   | 0.82 | 248                                   | 0.024                            |
| 10       | 17.1                                | 93                                   | 0.7  | 623  | 17   | 0.84 | 250                                   | 0.023                            |
| 12       | 17.2                                | 93                                   | 0.8  | 589  | 16   | 0.85 | 254                                   | 0.024                            |
| 14       | 17.1                                | 89                                   | 0.7  | 595  | 16   | 0.85 | 262                                   | 0.023                            |
| 16       | 17.2                                | 88                                   | 0.6  | 587  | 14   | 0.86 | 274                                   | 0.024                            |
| 18       | 17.2                                | 92                                   | 0.7  | 597  | 15   | 0.87 | 288                                   | 0.026                            |
| 20       | 17.4                                | 88                                   | 0.6  | 598  | 14   | 0.87 | 302                                   | 0.026                            |
| 22       | 17.3                                | 83                                   | 0.6  | 631  | 14   | 0.88 | 323                                   | 0.027                            |