

## Tables

Table 1: Preparation of 1L of  $\text{NH}_4\text{Cl}/\text{NH}_3$  and  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  buffer solutions.

Table 2: SPEs capacitive current obtained in  $\text{NaCl}$   $0.1 \text{ mol L}^{-1}$ . Experimental conditions: CV between  $0.1\text{V/NHE}$  and  $1\text{V/NHE}$ . Scan rate:  $0.05 \text{ V s}^{-1}$ , 5 electrodes.

Table 3:  $|\Delta E|$  (mV) as well as anodic and cathodic  $i_p$  (nA) measured by CV in  $\text{NaCl}$   $0.1 \text{ mol L}^{-1}$  containing  $\text{FcTMA}^+$   $2 \cdot 10^{-3} \text{ mol L}^{-1}$ . Experimental conditions: CV between  $0.1\text{V/NHE}$  and  $1\text{V/NHE}$ . Scan rate:  $0.05 \text{ V s}^{-1}$ , 5 electrodes.

Table 4: Results of the simulation of EIS measurements

Table 1

<b>NH<sub>4</sub>Cl/NH<sub>3</sub> buffer solutions</b>					
		Volume (mL) of		Total equivalent activity of	
	<b>pH</b>	HCl (1 mol L <sup>-1</sup> )	NH <sub>3</sub> (1 mol L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mol L <sup>-1</sup> )	NH <sub>3</sub> (mol L <sup>-1</sup> )
	7.2	50.0	50.7	3.4 10 <sup>-2</sup>	3.0 10 <sup>-4</sup>
	7.5	50.0	51.1	3.4 10 <sup>-2</sup>	6.3 10 <sup>-4</sup>
	7.6	50.0	50.3	3.4 10 <sup>-2</sup>	8.0 10 <sup>-4</sup>
	8.6	50.0	60.0	3.4 10 <sup>-2</sup>	8.0 10 <sup>-3</sup>
	9.3	50.0	97.0	3.3 10 <sup>-2</sup>	3.8 10 <sup>-2</sup>
	9.5	50.0	125.0	3.3 10 <sup>-2</sup>	5.9 10 <sup>-2</sup>
	9.7	50.0	170.0	3.2 10 <sup>-2</sup>	9.2 10 <sup>-2</sup>
	10.6	50.0	950.0	2.2 10 <sup>-2</sup>	4.5 10 <sup>-1</sup>
	10.8	30.0	970.0	1.4 10 <sup>-2</sup>	4.7 10 <sup>-1</sup>
<b>NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> buffer solutions</b>					
		Volume (mL) of		Total equivalent activity of	
IS*	<b>pH</b>	NaHCO <sub>3</sub> (1 mol L <sup>-1</sup> )	Na <sub>2</sub> CO <sub>3</sub> (1 mol L <sup>-1</sup> )	HCO <sub>3</sub> <sup>-</sup> (mol L <sup>-1</sup> )	CO <sub>3</sub> <sup>2-</sup> (mol L <sup>-1</sup> )
0.05	8.6	53.0	22.0	3.8 10 <sup>-2</sup>	1.2 10 <sup>-3</sup>
	8.9	43.0	3.6	3.1 10 <sup>-2</sup>	1.8 10 <sup>-3</sup>
	9.7	21.8	9.4	1.6 10 <sup>-2</sup>	4.7 10 <sup>-3</sup>
0.10	9.6	45.3	18.2	3.1 10 <sup>-2</sup>	8.3 10 <sup>-3</sup>
	10.1	24.9	22.3	1.8 10 <sup>-2</sup>	1.0 10 <sup>-2</sup>
	10.6	7.1	30.8	5.3 10 <sup>-3</sup>	1.4 10 <sup>-2</sup>
0.20	9.3	115.7	28.2		
	10.1	36.1	54.6		
	10.4	19.3	60.1		
	10.6	12.3	62.4		
	11.8	3.9	64.9		

\*IS: Ionic strength

Table 2

<b>SPEs</b>	<b>I<sub>c</sub> (nA)</b>
C	36 ± 1
CeO <sub>2</sub>	40 ± 2
Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub>	260 ± 10
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	470 ± 20

Table 3

<b>SPEs</b>	<b><math> \Delta E </math> (mV)</b>	<b><math>i_{pa}</math> (nA)</b>	<b><math>i_{pc}</math> (nA)</b>
C	$62 \pm 2$	$195 \pm 10$	$195 \pm 10$
CeO <sub>2</sub>	$63 \pm 3$	$205 \pm 10$	$205 \pm 10$
Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub>	$60 \pm 3$	$205 \pm 10$	$205 \pm 10$
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	$60 \pm 3$	$205 \pm 10$	$205 \pm 10$

Table 4

SPEs	EE Circuit	Component of the equivalent electrical circuit (EEC)					$\chi^2$
		$R_e$ (ohm)	$C_d$ ( $\mu\text{F}/\text{cm}^2$ )	$R_i$ (ohm)	Q-Yo ( $\times 10^6$ )	Q-n	
CeO <sub>2</sub>	R(C(RQ))	0.0	1.89	1587.0	0.556	0.927	0.0188
CeO <sub>2</sub>	R(CR)Q	0.0	1.89	1583.0	0.556	0.927	0.0187
Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub>	R(C(RQ))	0.0	0.63	5395.0	6.397	0.923	0.0073
Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub>	R(CR)Q	0.0	0.63	5395.0	6.397	0.923	0.0073
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	R(C(RQ))	0.0	0.31	19140.0	3.169	0.944	0.0088
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	R(CR)Q	0.0	0.31	19140.0	3.169	0.944	0.0088
C	R(C(RQ))	0.0	1.20	2316.0	0.487	0.920	0.0101
C	R(CR)Q	0.0	1.20	2313.0	0.488	0.920	0.0101